INVESTIGATIONS OF THE HIGH PRESSURE HYDROGENATION OF PHENOL AND THE CRESOLS WITH PLATINUM OXIDE CATALYST

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INVESTIGATIONS OF THE HIGH PRESSURE HYDROGENATION OF PHENOL AND THE CRESOLS WITH PLATINUM OXIDE CATALYST

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Arthur F. Miller

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INTRODUCTION

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There being no recorded kinetic investigation of the hydrogenation of cresols at high pressure with Adams platinum oxide catalyst, the purpose of the work described here was to make such a study. The problem was approached with the belief that a study of the rates of hydrogenation of such compounds and their stereoisomerism should give some insight into the mechanism of catalytic hydrogenation.

The compounds chosen for this study were phenol and the three isomeric cresols. The reaction medium used was ethyl alcohol with glacial acetic acid, and platinum oxide as a catalyst. Hydrogenations were carried out at an initial pressure of 1300 pounds per square inch and a temperature of 50° C.

HISTORY

HISTORY

The earliest recorded catalytic hydrogenation for the production of an organic compound is that by Debus (1) in 1863 in which he prepared methylamine by passing the vapors of hydrocyanic acid, mixed with hydrogen, over platinum black.

By the turn of the century catalytic hydrogenation began to be recognized as one of the major methods of chemical technique. This was due, in large measure, to the exhaustive researches of Sabatier and his associates, which are published in condensed form in Sabatier's book "La Catalyse en Chimie Organique"(2). Sabatier's process involves passing the organic substance, mixed with hydrogen, in the vapor phase over a nickel catalyst kept at the proper temperature, under a pressure of about one atmosphere.

Following, almost immediately, Sabatier's work, a second process for carrying out catalytic hydrogenations was introduced. This involved the reaction of hydrogen at one to five atmospheres pressure with the organic compound as a liquid or in solution in which the hydrogen and catalyst were agitated. Hydrogenation in the liquid phase became particularly useful with the development of colloidal platinum, platinum black (2), and platinum oxide or Adams' catalyst (3).

The catalytic reaction of hydrogen at high temperatures under pressures of 100 to 300 atmospheres with a compound in the liquid phase was introduced by Ipatieff (4) during the first decade of the present century.

The investigations of Armstrong and Hilditch (5) were the most systematic of the early work reported. Their results indicate, in the absence of disturbing factors, that the velocity of hydrogenation is directly proportional to the hydrogen pressure. Among these disturbing factors may be included slow acting permanent catalyst poisons, preferential adsorption of gaseous impurities at the catalyst surface, and the presence of a compound containing a functional group not susceptible to hydrogenation but having an affinity for the catalyst's surface.

Platinum oxide as a catalyst for the hydrogenation of the benzene nucleus at low pressure and moderate temperatures has been in rather general use for the past twenty-five years. Platinum is the actual catalyst when platinum oxide is used, as it is formed from the oxide as soon as hydrogen is introduced into the reaction vessel. The disadvantage of this catalyst is the ease with which it is poisoned by elementary sulfur or compounds containing divalent sulfur.

A qualitative study of the hydrogenation, using platinum oxide, of a number of phenyl substituted compounds was made by Adams and Marshall (6). Their results indicated increased difficulty of hydrogenation with increasing molecular complexity. In 1945, Smith and co-workers (7,8,9) made a quantitative study of the effect of structure on the hydrogenation of the benzene nucleus with Adams catalyst at low pressures. They showed that, under the experimental conditions employed,

the rate of hydrogenation was first order with respect to the hydrogen pressure, zero order with respect to the hydrogen acceptor, and directly proportional to the amount of catalyst used.

The first recorded use of Adams catalyst with high pressures was by Baker and Schuetz (10) in 1947. They demonstrated that the hydrogenation of benzenoid compounds followed essentially the same kinetics as at low pressure, although the time of hydrogenation was considerably less.

There are a number of references in the literature to the hydrogenation of the cresols. The interest in the cresols was due in large measure to the fact that the products of hydrogenation exist as geometrical isomers. In Table I is a summary of the stereoisomeric products obtained from the hydrogenation of the cresols and their corresponding methyl-cyclohexanones. In general, hydrogenation with nickel catalysts leads to predominantly trans isomers while platinum catalysts yield mainly the cis isomers.

TABLE I

STEREOISOMERISM OF THE HYDROGENATION PRODUCTS OF THE CRESOLS AND THEIR CORRESPONDING METHYLCYCLOHEXANONES

Compound Hydrogenated	Conditions	Hydrogenation Product
o-Cresol	Nickel at 175°C.	67% trans (11)
o-Cresol	Raney nickel at 180°C.	68% trans (12)
o-Cresol	Raney nickel at 100°C.	mainly trans (13)
o-Cresol	Pt black, acetic acid	mainly cis (14)
o-Cresol	Colloidal Pt, acetic acid	mainly cis (15)
o-Cresol	Copper chromite	100% trans (16)
m-Cresol	Nickel at 180°C.	82% trans (11)
m-Cresol	Raney nickel	mainly trans (17,13)
m-Cresol	Colloidal Pt, acetic acid	mainly cis (15)
m-Cresol	Copper chromite	100% cis (16)
p-Cresol	Raney nickel, 180°C.	82% trans (12)
p-Cresol	Raney nickel	mainly trans (13)
p-Cresol	Colloidal Pt, acetic acid	mainly cis (15)
2-Methylcyclohexanone	Sodium, moist ether	81% trans (11)
2-Methylcyclohexanone	Pt, acetic acid	62% cis (11)
2-Methylcyclohexanone	Raney nickel, 130°C.	57% cis (12)
2-Methylcyclohexanone	Pt black, acetic acid	mainly cis (14)
3-Methylcyclohexanone	Sodium, boiling alcohol	86% trans (11)
3-Methylcyclohexanone	Raney nickel	mainly cis (17)
3-Methylcyclohexanone	PTO_2, acetic acid	69% cis (17)
4-Methylcyclohexanone	Raney nickel, 130°C.	59% cis (12)

EXPERIMENTAL

EXPERIMENTAL

The materials used in a study of hydrogenations catalyzed by platinum oxide must necessarily be of high purity because of the poisoning effects of small amounts of foreign materials. The chemicals used in this work were:

Glacial acetic acid
Cyclohexene
Platinum oxide catalyst
Raney nickel catalyst
Ethyl alcohol
Phenol
o-cresol
m-cresol
p-cresol
Cyclohexanone
2-Methylcyclohexanone
3-Methylcyclohexanone
4-Methylcyclohexanone

The platinum oxide used in all hydrogenations in this investigation came from a single batch of catalyst obtained from the American Platinum Works. This eliminated the possibility of having a catalyst of varying activity.

The Raney nickel catalyst was prepared from a nickel-aluminum alloy, procured from the Central Scientific Company, following the method of Pavlic and Adkins (27). In a two-necked three-liter flask equipped with a stirrer and a thermometer, 128 grams (3.2 moles) of sodium hydroxide and 500 ml. of water were placed. The flask was immersed in cold running water and a 100 gram quantity of the alloy was added in small portions to the rapidly stirred solution, while maintaining the temperature at 50°C. After the addition of the alloy was complete, the suspension was digested for an hour on a water bath at 50°C., followed by washing with water until all alkali and water soluble salts had been removed. The resulting finely divided nickel was transferred to a 250 ml. centrifuge tube and washed three times by stirring with 95 per cent ethanol. The same procedure was followed with absolute ethanol to remove the last traces of water from the catalyst. The product was then stored under absolute ethanol.

Cyclohexene, Eastman's best grade, and glacial acetic acid, Baker's C. P. grade, were found suitable for use after distillation.

Ethyl alcohol of approximately 99.5 per cent purity was prepared as follows (18). A round-bottomed flask was filled to about two-thirds of its capacity with 95 per cent ethyl alcohol. Fresh quicklime, broken into lumps, was added to the alcohol using enough lime so that the pieces projected above its surface. A reflux condenser fitted with a calcium chloride drying tube was attached and the mixture was gently refluxed for an hour and then set aside for three days. Following this, the alcohol was again refluxed for an hour and then distilled directly into a suction flask protected with a calcium chloride tube against the entrance of moisture.

Phenol was obtained as a U.S.P. grade of material and was purified by distillation from Raney nickel to remove any trace of sulfur compounds.

o-Cresol, Eimer and Amend C.P. grade, was distilled from Raney nickel, as were m- and p-cresol, Eastman yellow label.

Cyclohexanone, Eastman white label grade, was distilled from Raney nickel.

The three isomeric methyl-cyclohexanones were prepared by dichromate oxidation of the alcohols which were obtained by the hydrogenation of the corresponding cresols. A hundred ml. quantity of the cresol was placed in the 185 ml. void Aminco high pressure hydrogenation bomb. To this was added one gram of sodium hydroxide, twenty ml. of ethyl alcohol and four grams of Raney nickel. The reaction mixture was shaken under an initial pressure of 3000 p.s.i. of hydrogen at 180°C. until there was no further pressure drop. The reduced product was decanted from the spent catalyst and neutralized with hydrochloric acid. The neutral solution was extracted three times with ethyl ether and the combined extracts were dried over magnesium sulfate. The ether and ethyl alcohol were removed by vacuum distillation. After distillation, the methylcyclohexanols were oxidised with a dichromate-sulfuric acid mixture (19).

In a one-liter round-bottomed flask provided with a mechanical stirrer was placed a solution containing 120 grams (0.4 moles) of sodium dichromate, 100 grams (54.3 ml., 0.97 moles) of concentrated sulfuric acid (sp. gr. 1.84) in 600 ml. of water. To this vigorously stirred mixture was added 0.58 moles of the methylcyclohexanol in four portions. Heat was evolved and the temperature of the reaction mixture rose to approximately 55°C., and then fell as soon as the reaction was complete. The resulting oily product was extracted with an equal volume of ether, separated, washed with three 200 ml. portions of 5% sodium hydroxide solution, then with water and dried over magnesium sulfate. After removal of the ether the methylcyclohexanones were obtained by distillation. They were given a final purification by redistillation from Raney nickel just prior to use.

The compounds hydrogenated were phenol, cyclohexanone, the three isomeric cresols, and their corresponding methylcyclohexanones. Each compound was hydrogenated at a temperature of 50°C. and an initial hydrogen pressure of 1300 pounds per square inch.

A standard American Instrument Company (Aminco) high pressure apparatus was used for these hydrogenations. The accompanying pressure gauge was graduated in divisions of ten pounds per square inch. Readings of elapsed time were made with a stop-watch. The readings were taken as the needle on the pressure gauge passed through the center of the division lines. A glass liner was used in all hydrogenations and consisted of a Pyrex ground glass tube fitted with a glass stopper which had a hole in the top to admit the hydrogen through a narrow tube. The latter was bent in a manner to minimize the loss of reaction mixture during shaking. The temperature was controlled and recorded by a Leeds and Northrup Micromax apparatus. The temperature during a hydrogenation was maintained constant with a variation of ± 1°C.

In carrying out the high pressure hydrogenations the general procedure was as follows. The catalyst and reactant, with the solvent, were placed in the glass liner which was then placed in the bomb after which it was sealed.

The bomb was next connected to the high pressure hydrogen source by means of a steel tube and hydrogen was allowed to flow slowly into the reaction vessel until the desired initial pressure was reached as indicated by the gauge. The bomb was then disconnected and placed in the shaker, keeping the open end of hydrogen delivery tube of the liner uppermost.

For obtaining initial pressures above those obtainable with commercial cylinders, a small hydraulic oil pump was used.

The volume, or hydrogen void, of the apparatus was determined by hydrogenating cyclohexene in acetic acid as a solvent. Assuming a quantitative hydrogenation of the olefinic double bond and using the ideal gas law, the hydrogen void was calculated to be 0.0481 liters (Table IX).

Each hydrogenation was carried out employing a mixture of approximately 0.02 moles of the compound to be hydrogenated, 0.1 gram of platinum oxide catalyst, 0.8 ml. of ethyl alcohol and 0.2 ml. of glacial acetic acid. A ratio of 0.194 moles of accepter per gram of catalyst was maintained throughout.

Thirty ml. each of o-cresol and 2-methylcyclohexanone were hydrogenated to determine the stereoisomerism of the products. When the hydrogen pressure had dropped to the calculated amount, the shaker was stopped and the remaining hydrogen was vented. After removing the liner from the bomb the reaction solution was filtered to recover the spent catalyst. The filtrate was stirred with dilute alkali to remove any traces of unreduced phenol, and with dilute sodium bisulfite to remove ketones. The solution was then extracted with ether and dried over anhydrous magnesium sulfate. Following removal of the ether the crude product was distilled in a small Claisen flask and the fraction boiling between 165°-170°C. was collected. Density and refractive index measurements were made on this mixture of isomeric 2-methylcyclohexanols before subjecting the mixture to fractionation in a Heli Grid Podbielniak column having a minimum of one hundred plates. The mixtures of alcohols obtained from o-cresol and 2-methylcyclohexanone were fractionated into six and eight cuts respectively under a pressure of 3 mm. Density and refractive index determinations were made on each of the fractions and are listed in Tables V and VI.

Since the presence of an intermediate ketone had been shown in the hydrogenation of phenolic compounds using Raney nickel as a catalyst in an alkaline medium (25), it was of interest to investigate the possibility of a similar intermediate using Adam's platinum oxide catalyst at high pressure in an acidic medium.

An attempt was made to detect the ketone intermediate by ultraviolet absorption spectra, using the Beckman D U spectrophotometer. Solutions of known concentrations of phenol and cyclohexanone in absolute ethyl alcohol were prepared and the per cent transmission at wave lengths between 260 millimicrons and 320 millimicrons were measured. It was determined that the concentrations required to obtain an appreciable absorption spectra with phenol was 10^{-4}N, and for cyclohexanone it was 10^{-2}N. It was also observed that the absorption peaks for both phenol

and cyclohexanone were very near to one another. Both of these findings were unfavorable, even before considering the effect of cyclohexanol. There is an adverse concentration factor. The amount of cyclohexanone present would have to be about one hundred times that of the phenol in order to contribute appreciably to the combined absorption spectra. Since such a high ratio of ketone to phenol was not anticipated, this method of detecting a possible ketone intermediate was given up.

Since deviations from first-order kinetics in the hydrogenation of phenols and the cresols had been observed after the hydrogenations were about two-thirds completed,the reaction products corresponding to two-thirds hydrogenation were investigated for the presence of ketones.

Samples of phenol and each of the three isomeric cresols were hydrogenated at high initial pressure in glacial acetic acid with platinum oxide to, a calculated, two-thirds completion. The reaction was then stopped and the catalyst filtered from the reaction mixture. The filtrate was neutralized with dilute sodium hydroxide and extracted with ether. The ether extract was dried over magnesium sulfate. After removal of the solvent, the remaining mixture of substances was fractionated using a small distillation flask equipped with a short Vigreux column. The distillate was collected in fractions of about half of a milliliter each. The ketone intermediate was shown to be present in one or more of these fractions resulting from the partial hydrogenation of phenol and each of the three isomeric cresols by the preparation and isolation of solid derivatives of each of the corresponding ketones. Table II lists the melting points of these derivatives.

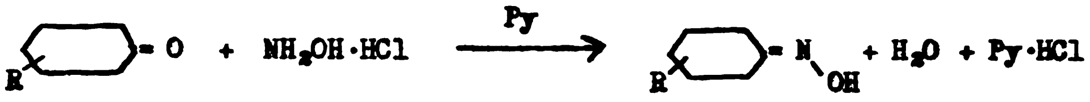
TABLE II

DERIVATIVES OF KETONES ISOLATED FROM THE PARTIAL HYDROGENATION OF SOME PHENOLS IN GLACIAL ACETIC ACID WITH PtO_2 AT HIGH PRESSURES

Phenol Hydrogenated	Ketone Intermediate	Derivative of Ketone	M. P. of Observed	Derivative Reported
Phenol	Cyclohexanone	2,4-D.N.P.[a]	162-3°	162° (23)
o-Cresol	2-Methylcyclohexanone	2,4-D.N.P.	136-7°	137° (23)
m-Cresol	3-Methylcyclohexanone	S.C.[b]	178-9°	178° (24)
p-Cresol	4-Methylcyclohexanone	S.C.	194-6°	196° (24)

a) 2,4-D.N.P. = 2,4-dinitrophenylhydrazone
b) S.C. = Semicarbazone

With the presence of the intermediate ketone in the hydrogenation of phenolic compounds in acid media with PtO_2 at high initial pressure confirmed, it was desirable to obtain a quantitative measure of the concentration of the intermediate ketone throughout the reaction. These determinations were made at intervals of each additional ten per cent hydrogenation starting at ten per cent hydrogenation. The method (26) used to determine quantitatively the amount of ketone present at any given per cent of complete hydrogenation was based on the determination of hydrogen chloride liberated in the formation of the ketoxime with hydroxylamine hydrochloride. The equations for the reactions involved are:



$$Py\cdot HCl + NaOH \xrightarrow[\text{blue}]{\text{bromphenol}} Py + NaCl + H_2O$$

where R = H or CH_3. Thus, the amount of hydrogen chloride liberated was a direct measure of the ketone present and could be determined by titration with a standard base, such as sodium hydroxide, using bromphenol blue as an indicator. The reagents used in this quantitative procedure were hydroxylamine hydrochloride, 95% ethyl alcohol, pyridine, and 4% alcoholic bromphenol blue solution. Approximately 0.5N hydroxylamine hydrochloride solution was prepared by dissolving 35 grams (0.5 moles) of the hydrochloride salt in 160 ml. of distilled water and diluting to one liter with 95% ethyl alcohol. The solvent mixture for the ketone containing sample was prepared by mixing 20 ml. of pyridine and one ml. of 4% alcoholic bromphenol blue solution and diluting to one liter with 95% ethyl alcohol. The standard sodium hydroxide solution was prepared by dissolving 20 grams (0.5 moles) of sodium hydroxide in 100 ml. of water and diluting to one liter with methyl alcohol. The alcoholic sodium hydroxide was standardized against potassium acid phthalate using phenolphthalein as an indicator.

In a pint pressure bottle, 30 ml. of the hydroxylamine hydrochloride solution was mixed with 100 ml. of the pyridine-indicator solution. To this was added a 5 ml. aliquot of the hydrogenation mixture, which had been made up to volume with ethyl alcohol in a 10 ml. volumetric flask. Sodium hydroxide was added to neutralize the acetic acid, the

equivalence point taken at the point where the color of the sample corresponded to that of the blank. The pressure bottles were then stoppered, placed in wire-mesh safety screens and heated on a steam bath for two hours, and then set aside to cool overnight. The sample solutions were then titrated with the standard sodium hydroxide solution to the same end point color as the blank which was identical to the hydrogenation samples except that it contained no ketone and had been treated in the same way as the samples. The results of these analyses are summarized in Tables XVIII to XXI.

Since the kinetic data obtained on the hydrogenation of phenol and the three isomeric cresols showed some deviations from a pseudo first-order rate expression as the hydrogenation progressed, it was decided to investigate the order of the reaction. This was done by holding constant all but one of the possible variables in the reaction and determining its effect on the reaction. The factors investigated were: amount of acid, amount of catalyst, initial hydrogen pressure, amount of acceptor, and rate of shaking. The results are tabulated in Tables VII and VIII.

CALCULATIONS AND RESULTS

CALCULATIONS AND RESULTS

It has been shown in several studies (10,21,22,23) that the hydrogenation of benzene derivatives over platinum oxide in the presence of glacial acetic acid is first order with respect to the hydrogen pressure, zero order with respect to the concentration of the hydrogen acceptor, and directly proportional to the amount of catalyst used. Thus, the rate of the reaction for a given amount of catalyst can be expressed by the differential equation

$$-\frac{d\,P_{H_2}}{dt} = k\,P_{H_2}$$

which, when integrated and expressed using logarithms on the base ten, gives

$$\log \frac{P^{o}_{H_2}}{P_{H_2}} = \frac{kt}{2.303}$$

where k is the specific reaction rate, t is the time, $P^{o}_{H_2}$ is the initial hydrogen pressure, and P_{H_2} is the hydrogen pressure at time t.

To calculate the values of the rate constant k, the slopes of the lines obtained by plotting $\log P^{o}_{H_2}/P_{H_2}$ against time were multiplied by 2.303. Since these constants were determined from different amounts of catalyst, they were referred to one gram of catalyst in order that all values may be comparable. The data and plots for the determination of the rate constants are shown in Tables X to XVII and Figures I-VIII in the Appendix. Since the hydrogenations of the ketones, cyclohexanone and the three methylcyclohexanones, did not obey the first order rate law under the conditions used to hydrogenate phenol and the isomeric cresols, a comparison of rate constants for the ketones investigated could not be made. The rate constants for phenol and the cresols are recorded in Table III.

TABLE III

SPECIFIC REACTION RATE CONSTANTS FOR THE HIGH PRESSURE HYDROGENATION* OF PHENOL AND THE THREE ISOMERIC CRESOLS

Acceptor	Moles	Grams of PtO_2	Initial Pressure (p.s.i.)	$k \times 10^{-3}$
Phenol	0.0228	0.1175	1300	11.6
o-Cresol	0.0194	0.1000	1300	8.32
m-Cresol	0.0191	0.0985	1300	10.3
p-Cresol	0.0192	0.0989	1300	10.4

*Hydrogenation carried out in a 0.0481 ml. Void Aminco Bomb in an Ethanol-Glacial Acetic Acid Solvent using PtO_2 as a Catalyst.

In order to determine the relative ease of hydrogenation of all the compounds studied, plots were made of the moles of acceptor hydrogenated against time and are shown in Figures IX-XVI. The times required for the initial 30% of hydrogenation of the acceptors are recorded in Table IV.

Since it has been shown by Jackman, Macbeth, and Mills (21) that a linear relationship exists between the densities of the isomeric

TABLE IV

TIMES REQUIRED FOR THE INITIAL THIRTY PER CENT OF HYDROGENATION IN THE HIGH PRESSURE HYDROGENATION* OF PHENOL, THE THREE ISOMERIC CRESOLS, CYCLOHEXANONE, AND THE THREE ISOMERIC METHYLCYCLOHEXANONES

Accepter	Moles	Grams of PtO_2	Initial Pressure (p.s.i.)	Time in Mins. for Initial 30% of Hydrogenation
Phenol	0.0228	0.1175	1300	12.4
Cyclohexanone	0.0197	0.0995	1300	8.0
o-Cresol	0.0194	0.1000	1300	13.5
2-Methylcyclohexanone	0.0152	0.0788	1300	11.1
m-Cresol	0.0191	0.0985	1300	12.7
3-Methylcyclohexanone	0.0159	0.0819	1300	8.5
p-Cresol	0.0192	0.0989	1300	12.7
4-Methylcyclohexanone	0.0149	0.0771	1300	8.4

* Hydrogenations carried out in a 0.0481 ml. Void Aminco Bomb in an Ethanol-Glacial Acetic Acid Solvent using PtO_2 as a catalyst.

2-methylcyclohexanols, the stereochemical structure of the 2-methylcyclohexanols resulting from the hydrogenation of o-cresol and 2-methylcyclohexanone was determined by density and refractive index measurements on the alcohols before and after distillation through a Heli Grid Podbielniak column at 3 mm Hg pressure. Measurement of the densities after a simple distillation and before fractionation indicated the per cent cis isomer in the hydrogenation of o-cresol was 75.2% and, in the case of 2-methylcyclohexanone, 77.2%. In Tables V and VI are shown the densities and refractive indices of the various fractions obtained by distillation using the Podbielniak column.

TABLE V

DENSITY AND REFRACTIVE INDEX MEASUREMENTS ON THE 2-METHYLCYCLOHEXANOL RESULTING FROM THE HIGH PRESSURE HYDROGENATION OF O-CRESOL IN AN ETHANOL-GLACIAL ACETIC ACID SOLVENT USING PtO_2 AS A CATALYST FRACTIONAL DISTILLATION WITH A HELI GRID PODBIELNIAK COLUMN

Fraction	Weight in Grams	n_{20} a)	D_{20} (g/ml) a)
1	5.7594	1.4647	0.9339
2	4.7502	1.4643	0.9334
3	4.7156	1.4640	0.9326
4	3.9864	1.4636	0.9315
5	2.3012	1.4633	0.9298
6	1.7416	1.4629	0.9282

a) Before fractionation D_{20} = 0.9313 and n_{20} = 1.4638.

TABLE VI

DENSITY AND REFRACTIVE INDEX MEASUREMENTS ON THE 2-METHYLCYCLOHEXANOL RESULTING FROM THE HIGH PRESSURE HYDROGENATION OF 2-METHYLCYCLOHEXANONE IN AN ETHANOL-GLACIAL ACETIC ACID SOLVENT USING PtO_2 AS A CATALYST FRACTIONAL DISTILLATION WITH A HELI GRID PODBIELNIAK COLUMN

Fraction	Weight in Grams	n_{20} b)	D_{20} b)
1	3.2360	1.4648	0.9338
2	6.2072	1.4645	0.9337
3	2.5072	1.4642	0.9334
4	2.8490	1.4640	0.9332
5	3.0990	1.4638	0.9328
6	3.6138	1.4635	0.9319
7	3.7126	1.4631	0.9300
8	1.4397	1.4628	0.9284

b) Before fractionation D_{20} = 0.9315, n_{20} = 1.4637

The plots of density against weight of alcohol distilled for these two hydrogenations are shown in Figure XVII. The reported values of the index of refraction and density (21,22) for cis-2-methylcyclohexanol are $n_{20} = 1.4649$; $D_{20} = 0.9336$ g/ml., and for trans-2-methylcyclohexanol are $n_{20} = 1.4616$; $D_{20} = 0.9237$.

It is evident that the product is predominantly the cis-isomer and that approximately the same percentage of cis-isomer is obtained from either o-cresol or its corresponding ketone.

The percent ketone present in the reaction mixtures at various degrees of hydrogenation are tabulated in Tables XVIII to XXI. Graphs showing the percent of ketone at various degrees of hydrogenation are found in Figures XVIII-XXI. Assuming there are no intermediates other than the respective ketones present in the reaction mixture, the amount of alcohol present can be calculated from the hydrogen uptake and the quantitative determination of the ketone by the hydroxylamine hydrochloride method. Since each mole of ketone formed has consumed two moles of hydrogen, the additional moles of hydrogen used divided by three yields the moles of alcohol. The moles of unreacted phenolic compound can be obtained by substracting the sum of the moles of ketone and alcohol from the moles of original phenolic compound. Graphs of the percent of components, phenolic compound, ketone, and alcohol, at various degrees of hydrogenation are shown in Figures XXII to XXV.

The data for the hydrogenation of phenol under different conditions are shown in Tables XXII to XXVI. Figure XXVI shows the plots of these hydrogenations according to first order kinetics. The values of the rate constants obtained from these plots are recorded in Table VII. Plots of the moles of phenol hydrogenated against time appear in Figure XXVII and the times for the initial 30% of hydrogenation are listed in Table VII.

The data for the hydrogenation of cyclohexanone as the conditions were varied are shown in Tables XXVII to XXXI. Plots of the moles of cyclohexanone hydrogenated against time appear in Figure XXVIII and the times for the initial 30% of hydrogenation are found in Table VIII.

When phenol or cyclohexanone were hydrogenated at a shaking rate of twenty-two cycles per minute, identical data was obtained as when these compounds were hydrogenated at the normal rate of thirty-four cycles per minute.

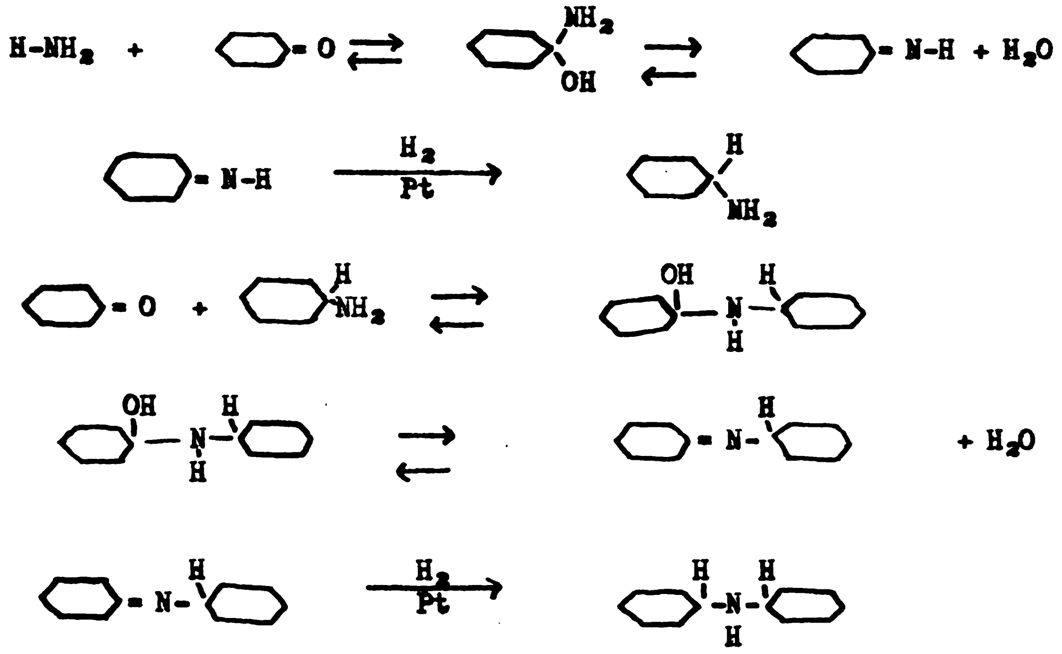
DISCUSSION

DISCUSSION

It had originally been planned to obtain kinetic data and information on the geometrical isomerism of the products resulting from the hydrogenation of o-cresol and 2-methylcyclohexanone in both acidic and basic solvents. A comparison of the specific reaction rates of hydrogenation and of the amounts of cis and trans 2-methylcyclohexanols obtained should give information as to whether the mechanism of hydrogenation was the same or different in the two media. Unfortunately, hydrogenation of the cresols in basic media could not be achieved. Among the bases investigated were sodium hydroxide, piperidine, and ammonium hydroxide. During periods of time of from eight to ten hours no appreciable drop in hydrogen pressure was obtained in any of these solvents. However, in each case, it was found that if the catalyst was washed and used in the hydrogenation of a fresh quantity of o-cresol in acetic acid, hydrogenation was obtained. This was accomplished by stopping the shaker after several hours, venting the hydrogen and recovering the catalyst by filtration. The catalyst was washed with water and alcohol before returning it to the reaction vessel with the fresh o-cresol in acetic acid as a solvent. It thus appears that the presence of a base poisoned the catalyst but such poisoning is not permanent since it could easily be removed from the catalyst by washing.

When the ketones were hydrogenated under similar conditions in the presence of ammonium hydroxide, a rapid drop in hydrogen pressure

was observed. This reductive amination took place at a faster rate than the hydrogenation of the corresponding phenolic compounds. The course of the reductive amination can be represented as follows:



The presence of cyclohexylamine and dicyclohexylamine was confirmed by the preparation of their hydrochlorides following fractional distillation of the hydrogenation products of cyclohexanone in ammoniacal media.

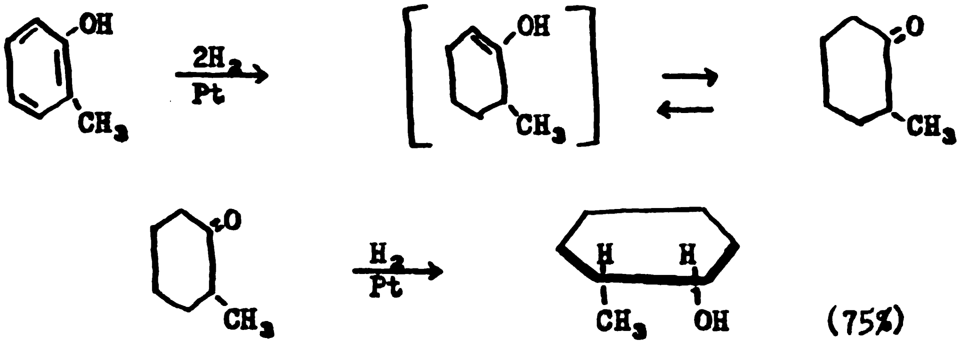
Since the hydrogenation of the ketones in ammoniacal solution proceeds readily, it is evident that the poisoning of the catalyst observed in the case of the phenols was selective. This could be explained either on the basis of the relative attraction of the base and the acceptor for the same type of active centers on the catalyst surface or by considering the catalyst to have more than one type of active centers. It is possible that ammonia is held to the catalyst by stronger forces than phenols and does not permit the latter to replace it. The Schiff base type of compound resulting from the reaction of the ketone with ammonia may be able to replace the ammonia on the catalyst, or the ketone may react with both the ammonia and the hydrogen at the catalyst surface.

The geometry of the active centers may also account for the selectivity of basic poisoning. Phenols, as well as other aromatic compounds, have been found to hydrogenate only on certain types of catalysts (28), namely, those which have a certain geometrical pattern of active centers. The flat wise adsorption of phenol could be prevented by the contamination of some of these centers by the base while a ketimine would require only two adjacent active centers on the catalyst.

Since the rather extreme conditions, for Adams platinum oxide catalyst, of 1300 pounds per square inch hydrogen pressure and 50°C. had been used with the phenols in attempting to carry out their hydrogenation in basic media, it was decided to investigate their hydrogenation in acidic media under similar conditions of initial pressure and temperature. Under these conditions both the phenolic compounds and their corresponding ketones were hydrogenated.

Considering first the geometrical configuration of the alcohols obtained from the hydrogenation of o-cresol and 2-methylcyclohexanone, it was found that in both cases approximately seventy-five per cent cis-2-methylcyclohexanol was obtained. This indicated that, in the hydrogenation of o-cresol, the ketone occurred as an intermediate.

The reactions involved could be represented by the following equations:



The specific reaction rate constants for the hydrogenation of the cresols and of their corresponding methylcyclohexanones could not be compared since the ketones did not follow first order kinetics.

A further indication that the ketone is an intermediate in the hydrogenation of the phenols is shown in the plot of the hydrogenation of the phenols according to first order kinetics. The initial portion of the curves, to about seventy per cent, is a straight line in every case. However, the remaining portion of the hydrogenation curve shows a deviation from this straight line. This presumably could be due to the relatively higher concentration of the ketone than of the phenolic compound at this stage of the hydrogenation as is shown in Figures XXII to XXV.

The actual physical presence of the ketone intermediate in the reaction mixture was shown by interrupting the hydrogenation at sixty to seventy per cent of completion and subjecting the reaction mixture to fractional distillation. For phenol and the three cresols a sufficient amount of the corresponding ketone was obtained in each case to prepare

and isolate solid derivatives, thus confirming the presence of the intermediate ketones.

Since the rate curves for the hydrogenation of the phenols did not follow first order kinetics throughout the latter part of the hydrogenation, it was of interest to determine the composition of the reaction mixture as hydrogenation progressed. Assuming the ketone to be the only stable intermediate formed, the composition of the reaction mixture at any particular degree of hydrogenation could be expressed in terms of moles of phenol, ketone, and alcohol. Figures XXII to XXV show that above sixty percent hydrogenation the concentration of ketone present is greater than that of the phenol. Thus, since the ketones did not follow first order kinetics, it is not surprising that the composite curve for the hydrogenation of phenols and their ketone intermediates are found to deviate from first order.

A comparison of the relative rates for the hydrogenation of phenol and the cresols can be made. The order found was, phenol > p-cresol = m-cresol > o-cresol. These results can be accounted for from a consideration of steric hindrance. This may be of two types. First, the steric hindrance between the catalyst and the adsorbed molecules, and, secondly, steric hindrance of the type which interferes with the approach of hydrogen molecules to the catalytic surface. In the first instance, flat adsorption of the benzene ring requires that the molecule find an area on the catalyst which has sufficient size and suitable spacing of the metallic atoms. Substituents on the benzene ring would be expected to decrease the possible number of areas where the molecule could be adsorbed. Adjacent substituents have been found to decrease the rate of hydrogenation to a greater degree than the same number of nonadjacent substituents (7).

The second type of steric hindrance might be important in governing the rate, since the hydrogen must pass through the substituents which extend away from the catalytic surface following adsorption of the acceptor, in order to be adsorbed and subsequently react. The rate at which hydrogen is adsorbed on the catalyst may be rate determining for the hydrogenation process. This would be in line with first order rate dependence on hydrogen pressure.

In order for the intermediate ketone to be isolated, the partially hydrogenated phenol molecule must have left the catalyst surface. Since the ketone must then be readsorbed on the catalyst for the final stage of the hydrogenation, steric effects could come into play at this point. The hydrogenation of the ketone can be pictured as involving adsorption of the carbonyl group only. Here again, an ortho substituent could hinder the approach of the carbonyl group to the catalyst surface. This effect would not be as great in the adsorption of the 3- and 4-methylcyclohexanones.

Since the ketones did not yield straight lines when plotted according to first order kinetics, the rate constants could not be obtained. In order to have a basis for the comparison of the relative ease of hydrogenation of the ketones, the time required for the initial thirty per cent of hydrogenation was determined from plots of the moles of ketone hydrogenated against time. The relative order found was,

cyclohexanone > 4-methylcyclohexanone > 3-methylcyclohexanone > 2-methylcyclohexanone. When the same comparison, that is, time required for thirty per cent hydrogenation, was applied to phenol and the cresols, the same relative order as that obtained by comparison of rate constants resulted, as is shown in Tables III and IV.

The effect of varying the conditions in the hydrogenation of phenol provides evidence that the hydrogenation of phenol follows a first order rate expression for approximately three-fourths of the hydrogenation. As is shown in Table VII, decreasing the amount of acid by one half had no appreciable effect on the time required for the initial thirty per cent of the hydrogenation and no effect on the rate constant. When the amount of catalyst was increased or decreased, there were changes in both the time and rate constant in all cases in the expected direction. Decreasing the initial hydrogen pressure by a factor of two approximately doubled the time required while the rate constant remained unchanged. Decreasing the concentration of acceptor by a facter of two had no effect on the rate constant and the time required was halved. The hydrogenation of phenol can thus be considered to be independent of the concentration of acid used, proportional to the amount of catalyst used, independent of the concentration of the acceptor, and first order with respect to hydrogen pressure.

The effects of changing the conditions in the hydrogenation of cyclohexanone follow the same pattern as with phenol except in the case where the initial hydrogen pressure was halved as shown in Table VIII. An increase in the time required for the initial thirty per cent of hydrogenation was noted but the increase was considerably less than a factor of two as was found in the case of phenol. Since cyclohexanone did not follow first order kinetics during the hydrogenation, this deviation is not surprising.

It should be noted that all the data for the hydrogenations of the phenolic compounds represents the composite effects of the two stages of hydrogenation taking place simultaneously. Variations in the data from what would be predicted for a single step hydrogenation which follows first order kinetics may be attributed to this fact.

SUMMARY

SUMMARY

1. Specific reaction rate constants have been determined for the high pressure hydrogenation of phenol and the three isomeric cresols using platinum oxide catalyst.

2. The time required for the initial thirty per cent of hydrogenation of phenol, cyclohexanone, the three isomeric cresols, and their corresponding methylcyclohexanones have been determined.

3. The hydrogenation products of o-cresol and 2-methylcyclohexanone were shown to have the same ratio of cis-2-methylcyclohexanol to trans-2-methylcyclohexanol. In both cases the hydrogenation products contained seventy-five per cent of the cis isomer.

4. The presence of an intermediate ketone in the hydrogenation of phenol and the three isomeric cresols was confirmed by the preparation and isolation of solid derivatives of the corresponding ketones in each case. In addition, the concentration of the ketone throughout the hydrogenations was determined quantitatively. The hydrogenation of the phenolic compounds investigated were thus shown to undergo hydrogenation in a step-wise manner.

5. It was concluded that the ketone intermediates did not follow first-order kinetics under the hydrogenation conditions investigated.

6. The deviation from first-order kinetics for the phenolic compounds investigated as hydrogenation progressed was explained on the basis of a higher concentration of ketone than of phenolic compound in the reaction mixture in the final phase of hydrogenation.

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LITERATURE CITED

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APPENDIX

TABLE VII

SPECIFIC REACTION RATE CONSTANTS AND TIME REQUIRED FOR THE INITIAL THIRTY PER CENT HYDROGENATION OF PHENOL IN A 48.1 ML. VOID AMINCO BOMB USING PtO_2 AS A CATALYST IN AN ETHANOL-GLACIAL ACETIC ACID SOLVENT

EFFECT OF VARYING THE CONDITIONS

Moles of Phenol	Grams of PtO_2	Initial Hydrogen Pressure (p.s.i.)	Ml. of Glacial Acetic Acid	k (Reciprocal Minutes x 10^{-2})	Time in Minutes for Initial 30% Hydrogenation
0.0228	0.1175	1300	0.2	11.6	12.4
0.0228	0.1175	1300	0.1	11.6	12.4
0.0228	0.2350	1300	0.2	13.7	9.9
0.0228	0.0588	1300	0.2	9.7	14.8
0.0228	0.1175	650	0.2	11.9	27.1
0.0114	0.1175	1300	0.2	11.6	6.0

TABLE VIII

SPECIFIC REACTION RATE CONSTANTS AND TIME REQUIRED FOR THE INITIAL THIRTY PER CENT HYDROGENATION OF CYCLOHEXANONE IN A 48.1 ML. VOID AMINCO BOMB USING PtO_2 AS A CATALYST IN AN ETHANOL-GLACIAL ACETIC ACID SOLVENT

EFFECT OF VARYING THE CONDITIONS

Moles of Cyclohexanone	Grams of PtO_2	Initial Hydrogen Pressure (p.s.i.)	Ml. of Glacial Acetic Acid	Time in Minutes for Initial 30% Hydrogenation
0.0197	0.0995	1300	0.2	8.0
0.0197	0.0995	1300	0.1	8.4
0.0197	0.1990	1300	0.2	4.0
0.0197	0.0498	1300	0.2	13.8
0.0197	0.0995	650	0.2	9.8
0.0099	0.0995	1300	0.2	4.2

TABLE IX

Cyclohexene
0.0394 Moles

High Pressure
0.1000 g. PtO_2

0.5 ml. of acetic acid

Time (Minutes)	Temperature (Degrees C.)	Pressure (p.s.i.)	Log Po/p
0.0	23	1300	--
1.0	23	1135	--
1.5	24	1115	--
3.3	24	1095	--
20.6	23	985	--
47.5	23	980	--
62.3	23	980	--

TABLE X

Phenol — High Pressure
0.0228 Moles — 0.1175 g. PtO_2
0.2 ml. of acetic acid, 0.8 ml. of ethyl alcohol

Time (Minutes)	Temperature (Degrees C.)	Pressure (p.s.i.)	Moles Compd. Hydrogenated	Log Po/P
0.0	50	1300	.0000	.000
2.8	50	1255	.0018	.015
7.1	51	1195	.0042	.037
10.2	50	1155	.0058	.050
14.8	50	1095	.0081	.075
17.8	51	1055	.0097	.091
24.1	51	975	.0120	.116
35.5	50	855	.0176	.182
45.3	50	795	.0199	.214
52.2	50	775	.0207	.225

TABLE XI

Cyclohexanone
0.0197 Moles
High Pressure
0.0995 g. PtO_2
0.2 ml. of acetic acid, 0.8 ml. of ethyl alcohol

Time (Minutes)	Temperature (Degrees C.)	Pressure (p.s.i.)	Moles Compd. Hydrogenated	Log Po/P
0.0	50	1300	.0000	.000
1.6	50	1285	.0018	.005
3.0	50	1275	.0029	.008
6.9	50	1255	.0052	.015
11.6	50	1235	.0075	.022
16.1	50	1215	.0099	.029
23.6	50	1195	.0122	.037
33.2	50	1175	.0145	.044
47.5	50	1155	.0168	.050

TABLE XII

o-Cresol
0.0194 Moles

High Pressure
0.1000 g. PtO_2

0.2 ml. of acetic acid, 0.8 ml. of acetic acid

Time (Minutes)	Temperature (Degrees C.)	Pressure (p.s.i.)	Moles Compd. Hydrogenated	Log Po/P
0.0	50	1300	.0000	.000
1.9	50	1275	.0010	.008
9.2	51	1195	.0041	.037
14.7	50	1135	.0064	.059
23.6	50	1045	.0098	.095
28.7	50	990	.0113	.112
36.6	50	965	.0129	.129
42.8	49	945	.0137	.138
46.0	50	935	.0140	.143
52.0	50	915	.0146	.153
60.8	50	895	.0156	.162
116.5	50	815	.0187	.203

TABLE XIII

2-Methylcyclohexanone
0.0152 moles

High Pressure
0.0788 g. PtO_2

0.2 ml. of acetic acid, 0.8 ml. of ethyl alcohol

Time (Minutes)	Temperature (Degrees C.)	Pressure (p.s.i.)	Moles Compd. Hydrogenated	Log Po/P
0.0	50	1300	.0000	.000
1.0	50	1295	.0006	.002
2.4	49	1285	.0017	.005
5.5	50	1275	.0028	.008
8.6	50	1265	.0040	.012
13.8	50	1255	.0051	.015
18.3	50	1245	.0062	.019
31.4	50	1225	.0085	.026
42.0	50	1215	.0100	.029
54.8	50	1205	.0107	.033

TABLE XIV

m-Cresol	High Pressure
0.0191 Moles	0.0985 g. PtO_2
0.2 ml. of acetic acid, 0.8 ml. of ethyl alcohol

Time (Minutes)	Temperature (Degrees C.)	Pressure (p.s.i.)	Moles Compd. Hydrogenated	Log Po/P
0.3	50	1300	.0000	.000
1.3	50	1285	.0006	.005
5.3	50	1235	.0025	.022
10.1	51	1175	.0047	.044
17.0	50	1095	.0078	.075
26.8	50	985	.0123	.121
30.1	50	955	.0131	.134
35.0	50	915	.0146	.153
39.0	50	895	.0153	.162
44.6	49	875	.0161	.172

TABLE XV

3-Methylcyclohexanone — **High Pressure**
0.0159 Moles — **0.0819 g. PtO_2**
0.2 ml. of acetic acid, 0.8 ml. of ethyl alcohol

Time (Minutes)	Temperature (Degrees C.)	Pressure (p.s.i.)	Moles Compd. Hydrogenated	Log Po/P
0.0	50	1300	.0000	.000
0.9	50	1295	.0006	.002
2.2	50	1285	.0017	.005
4.2	50	1275	.0029	.008
6.3	50	1265	.0040	.012
12.6	50	1245	.0063	.019
19.0	50	1225	.0085	.026
27.8	49	1205	.0108	.033
34.0	50	1195	.0119	.037

TABLE XVI

p-Cresol
0.0192 Moles

High Pressure
0.0989 g. PtO_2

0.2 ml. of acetic acid, 0.8 ml. of ethyl alcohol

Time (Minutes)	Temperature (Degrees C.)	Pressure (p.s.i.)	Moles Compd. Hydrogenated	Log Po/P
0.0	50	1300	.0000	.000
3.6	51	1255	.0017	.015
6.9	50	1215	.0033	.029
15.1	50	1115	.0071	.067
22.3	49	1035	.0102	.099
32.6	50	935	.0140	.143
39.8	50	895	.0156	.162
46.1	50	875	.0163	.172
50.2	49	865	.0167	.177
58.0	50	855	.0171	.182

TABLE XVII

4-Methylcyclohexanone
0.0149 Moles

High Pressure
0.0771 g. PtO_2

0.2 ml. of acetic acid, 0.8 ml. of ethyl alcohol

Time (Minutes)	Temperature (Degrees C.)	Pressure (p.s.i.)	Moles Compd. Hydrogenation	Log Po/P
0.0	50	1300	.0000	.000
0.9	50	1295	.0006	.002
2.1	50	1285	.0018	.005
4.7	50	1275	.0030	.008
7.6	50	1265	.0042	.012
11.4	50	1255	.0054	.015
13.4	49	1245	.0066	.019
19.3	50	1235	.0076	.022
24.1	50	1225	.0089	.026
29.2	50	1215	.0101	.029
36.4	50	1205	.0113	.033

TABLE XVIII

Percent Hydrogenation	Moles of Cyclohexanone	Percent of Cyclohexanone	Moles of Cyclohexanol	Percent of Cyclohexanol	Moles of Phenol	Percent of Phenol
0	.0000	0.0	.0000	0.0	.0228	100.0
10	.0022	9.8	.0008	3.5	.0198	87.0
20	.0041	19.3	.0016	7.2	.0168	73.7
30	.0058	25.2	.0030	13.1	.0140	61.4
40	.0075	32.7	.0042	18.2	.0112	49.1
50	.0081	35.5	.0060	26.3	.0087	38.2
60	.0085	37.4	.0079	34.6	.0064	28.1
70	.0087	37.9	.0102	44.7	.0039	17.1
80	.0085	37.1	.0126	55.3	.0017	7.5
90	.0050	22.0	.0172	75.4	.0006	2.6

TABLE XIX

Percent Hydrogenation	Moles of 2-Methyl-Cyclohexanone	Percent of 2-Methyl-Cyclohexanone	Moles of 2-Methyl-Cyclohexanol	Percent of 2-Methyl-Cyclohexanol	Moles of o-Cresol	Precent of o-Cresol
0	.0000	0.0	.0000	0.0	.0194	100.0
10	.0024	12.2	.0003	1.7	.0167	86.0
20	.0040	20.6	.0012	6.2	.0142	73.2
30	.0053	27.2	.0023	11.8	.0118	60.8
40	.0072	37.1	.0030	15.3	.0092	47.4
50	.0081	41.7	.0043	22.3	.0070	36.1
60	.0080	40.4	.0063	32.7	.0051	26.3
70	.0072	37.2	.0088	45.2	.0034	17.5
80	.0060	31.0	.0112	57.7	.0022	11.4
90	.0034	17.6	.0153	79.0	.0007	3.6

TABLE IX

Percent Hydrogenation	Moles of 3-Methyl-Cyclohexanone	Percent of 3-Methyl-Cyclohexanone	Moles of 3-Methyl-Cyclohexanol	Percent of 3-Methyl-Cyclohexanol	Moles of m-Cresol	Percent of m-Cresol
0.0	.0000	0.0	.0000	0.0	.0191	100.0
10.0	.0022	11.7	.0004	2.3	.0164	85.9
20.0	.0032	16.5	.0017	9.1	.0142	74.5
30.0	.0043	22.3	.0029	15.3	.0119	62.3
40.0	.0051	26.4	.0043	22.6	.0097	50.8
50.0	.0059	31.0	.0056	29.4	.0076	39.8
60.0	.0062	32.2	.0074	38.9	.0055	28.8
70.0	.0063	33.1	.0092	48.3	.0035	18.3
80.0	.0040	20.9	.0127	66.5	.0024	12.6
90.0	.0013	6.9	.0163	85.4	.0015	7.8

TABLE XXI

Percent Hydrogenation	Moles of 4-Methyl-Cyclohexanone	Percent of 4-Methyl-Cyclohexanone	Moles of 4-Methyl-Cyclohexanol	Percent of 4-Methyl-Cyclohexanol	Moles of p-Cresol	Percent of p-Cresol
0	.0000	0.0	.0000	0.0	.0192	100.0
10	.0016	8.4	.0008	4.4	.0167	87.0
20	.0029	15.3	.0019	9.8	.0144	75.0
30	.0035	18.3	.0034	17.7	.0123	64.1
40	.0046	24.2	.0046	23.9	.0100	52.0
50	.0054	28.0	.0060	31.4	.0078	40.6
60	.0064	33.4	.0072	37.6	.0055	28.8
70	.0060	31.4	.0094	49.1	.0037	19.3
80	.0044	22.9	.0124	64.6	.0024	12.5
90	.0019	10.0	.0160	83.5	.0013	6.7

TABLE XXII

Phenol — High Pressure

0.0228 Moles — 0.1175 g. PtO_2

0.1 ml. of acetic acid, 0.9 ml. of ethyl alcohol

Time (Minutes)	Temperature (Degrees C.)	Pressure (p.s.i.)	Moles Compd. Hydrogenation	Log Po/P
0.0	50	1300	.0000	.000
1.2	50	1285	.0006	.005
3.0	50	1255	.0018	.015
4.3	51	1235	.0026	.022
7.4	51	1195	.0042	.037
10.4	50	1155	.0058	.050
13.5	50	1115	.0073	.067
16.7	50	1075	.0089	.083
19.8	49	1035	.0105	.099
23.0	50	995	.0120	.116
28.5	50	935	.0144	.143
34.6	50	875	.0167	.172

TABLE XXIII

Phenol
0.0228 Moles

High Pressure
0.2350 g. PtO_2

0.2 ml. of acetic acid, 0.8 ml. of ethyl alcohol

Time (Minutes)	Temperature (Degrees C.)	Pressure (p.s.i.)	Moles Compd. Hydrogenated	Log Po/P
0.0	50	1300	.0000	.000
0.9	50	1285	.0006	.005
1.9	50	1255	.0018	.015
2.7	50	1235	.0026	.022
5.1	51	1195	.0042	.037
7.8	50	1155	.0058	.050
10.7	50	1115	.0073	.067
13.8	50	1075	.0089	.083
16.8	50	1035	.0105	.099
19.7	50	995	.0120	.116
24.5	50	935	.0144	.143
29.5	50	275	.0167	.172

TABLE XXIV

Phenol High Pressure
0.0228 Moles 0.0588 g. PtO_2
0.2 ml. of acetic acid, 0.8 ml. of ethyl alcohol

Time (Minutes)	Temperature (Degrees C.)	Pressure (p.s.i.)	Moles Compd. Hydrogenated	Log Po/P
0.0	50	1300	.0000	.000
1.1	50	1285	.0006	.005
3.3	50	1255	.0018	.015
5.0	50	1235	.0026	.022
8.4	51	1195	.0042	.037
12.2	50	1155	.0058	.050
15.9	50	1115	.0073	.067
19.2	50	1075	.0089	.083
23.9	50	1035	.0105	.099
31.7	50	955	.0136	.134
38.3	50	895	.0160	.162

TABLE XXV

Phenol — **High Pressure**

0.0228 Moles — 0.1175 g. PtO_2

0.2 ml. of acetic acid, 0.8 ml. of ethyl alcohol

Time (Minutes)	Temperature (Degrees C.)	Pressure (p.s.i.)	Moles Compd. Hydrogenated	Log Po/P
0.0	50	650	.0000	.000
4.2	50	615	.0014	.024
6.4	50	595	.0021	.038
9.7	50	575	.0029	.053
12.3	49	555	.0037	.069
15.7	50	535	.0045	.085
19.0	50	515	.0052	.101
23.1	50	495	.0060	.118
30.4	50	455	.0075	.155
42.1	50	395	.0099	.216

TABLE XXVI

Phenol **High Pressure**
0.0114 Moles **0.1175 g. PtO_2**
0.2 ml. of acetic acid, 0.8 ml. of ethyl alcohol

Time (Minutes)	**Temperature (Degrees C.)**	**Actual Pressure (p.s.i.)**	**Moles Compd. Hydrogenated**	**Log Po/P**
0.0	50	1300	.0000	.000
1.6	50	1275	.0010	.008
4.4	50	1235	.0025	.022
6.0	50	1215	.0033	.029
8.9	50	1175	.0048	.044
11.7	50	1135	.0064	.059
15.1	49	1095	.0079	.075
17.0	50	1075	.0087	.083
19.5	50	1055	.0095	.091

TABLE XXVII

Cyclohexanone
0.0197 Moles

High Pressure
0.0995 g. PtO_2

0.1 ml. of acetic acid, 0.9 ml. of ethyl alcohol

Time (Minutes)	Temperature (Degrees C.)	Actual Pressure (p.s.i.)	Moles Compd. Hydrogenated	Log Po/P
0.0	50	1300	.0000	.000
1.7	50	1285	.0018	.005
3.1	51	1275	.0029	.008
7.2	51	1255	.0052	.015
11.8	50	1235	.0075	.022
16.4	50	1215	.0099	.029
24.0	50	1195	.0122	.037
34.1	50	1175	.0145	.044
49.3	50	1155	.0168	.050

TABLE XXVIII

Cyclohexanone High Pressure
0.0197 Moles 0.1990 g. PtO_2
0.2 ml. acetic acid, 0.8 ml. of ethyl alcohol

Time (Minutes)	Temperature (Degrees C.)	Actual Pressure (p.s.i.)	Moles Compd. Hydrogenated	Log Po/P
0.0	50	1300	.0000	.000
1.2	50	1285	.0018	.005
1.7	50	1275	.0029	.008
3.4	50	1255	.0052	.015
5.6	50	1235	.0075	.022
9.1	50	1215	.0099	.029
13.7	50	1195	.0122	.037
18.7	50	1175	.0145	.044
25.2	50	1155	.0168	.050

TABLE XXIX

Cyclohexanone 0.0197 Moles — High Pressure 0.0498 g. PtO_2

0.2 ml. of acetic acid, 0.8 ml. of ethyl alcohol

Time (Minutes)	Temperature (Degrees C.)	Actual Pressure (p.s.i.)	Moles Compd. Hydrogenated	Log Po/P
0.0	50	1300	.0000	.000
1.7	50	1285	.0018	.005
3.3	50	1275	.0029	.008
11.0	49	1255	.0052	.015
20.2	50	1235	.0075	.022
28.8	50	1215	.0099	.029
43.9	50	1195	.0122	.037
50.6	50	1185	.0133	.040
58.0	50	1175	.0145	.044

TABLE XXX

Cyclohexanone
0.0197 Moles

High Pressure
0.0995 g. PtO_2

0.2 ml. of acetic acid, 0.8 ml. of ethyl alcohol

Time (Minutes)	Temperature (Degrees C.)	Actual Pressure (p.s.i.)	Moles Compd. Hydrogenated	Log Po/P
0.0	50	650	.0000	.000
1.4	50	635	.0017	.010
5.4	50	615	.0041	.024
11.2	50	595	.0064	.038
17.4	51	575	.0087	.053
25.2	50	555	.0110	.069
35.1	50	535	.0134	.085
44.5	50	515	.0156	.101

TABLE XXXI

Cyclohexanone — High Pressure
0.0099 Moles — 0.0995 g. PtO_2
0.2 ml. of acetic acid, 0.8 ml. of ethyl alcohol

Time (Minutes)	Temperature (Degrees C.)	Actual Pressure (p.s.i.)	Moles Compd. Hydrogenation	Log Po/P
0.0	50	1300	.0000	.000
1.4	50	1285	.0018	.005
4.5	50	1275	.0029	.008
7.5	51	1265	.0041	.012
12.9	50	1255	.0053	.015
18.1	50	1245	.0064	.019
26.0	50	1235	.0076	.022
36.4	50	1225	.0087	.026

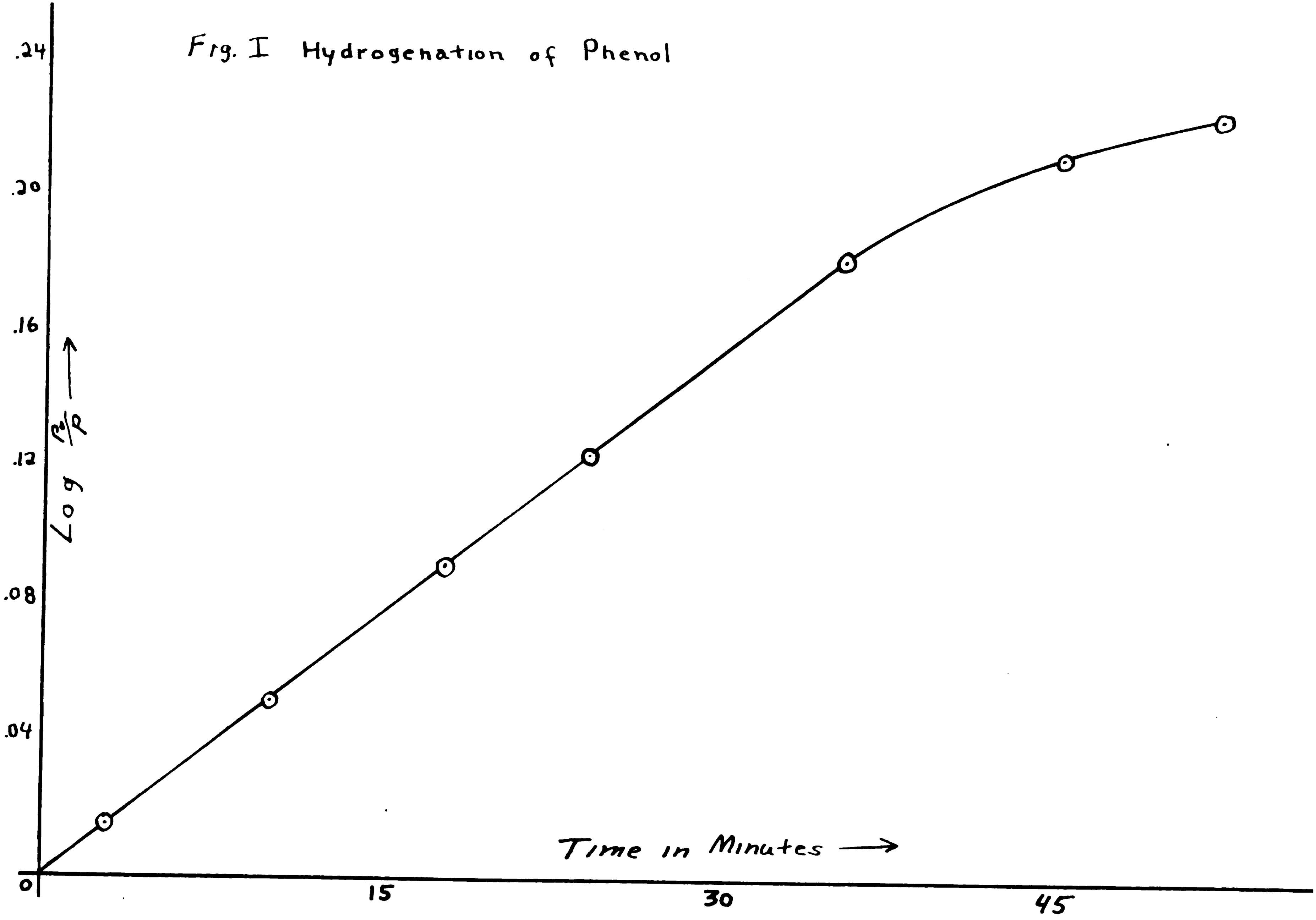


Fig. I Hydrogenation of Phenol

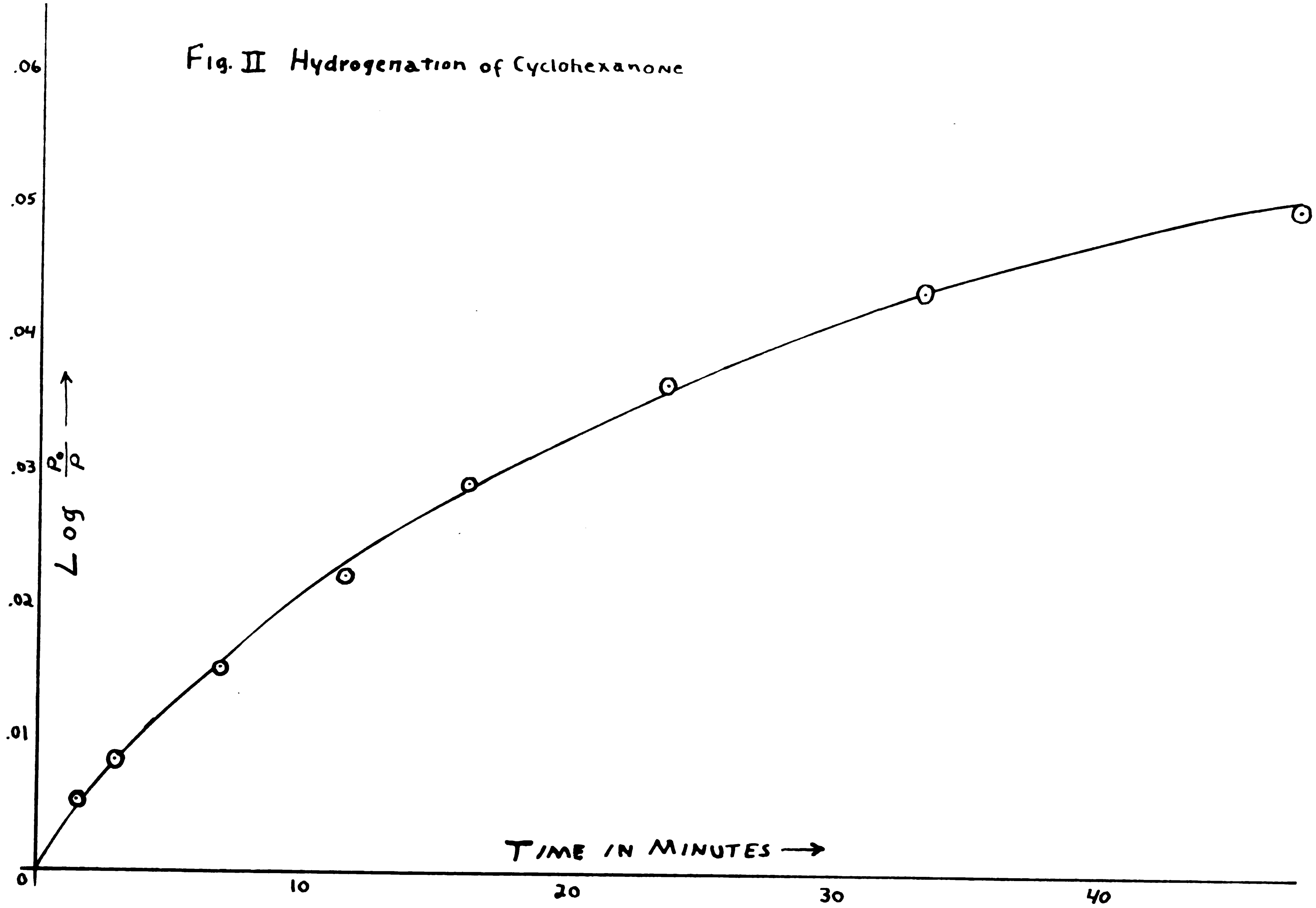
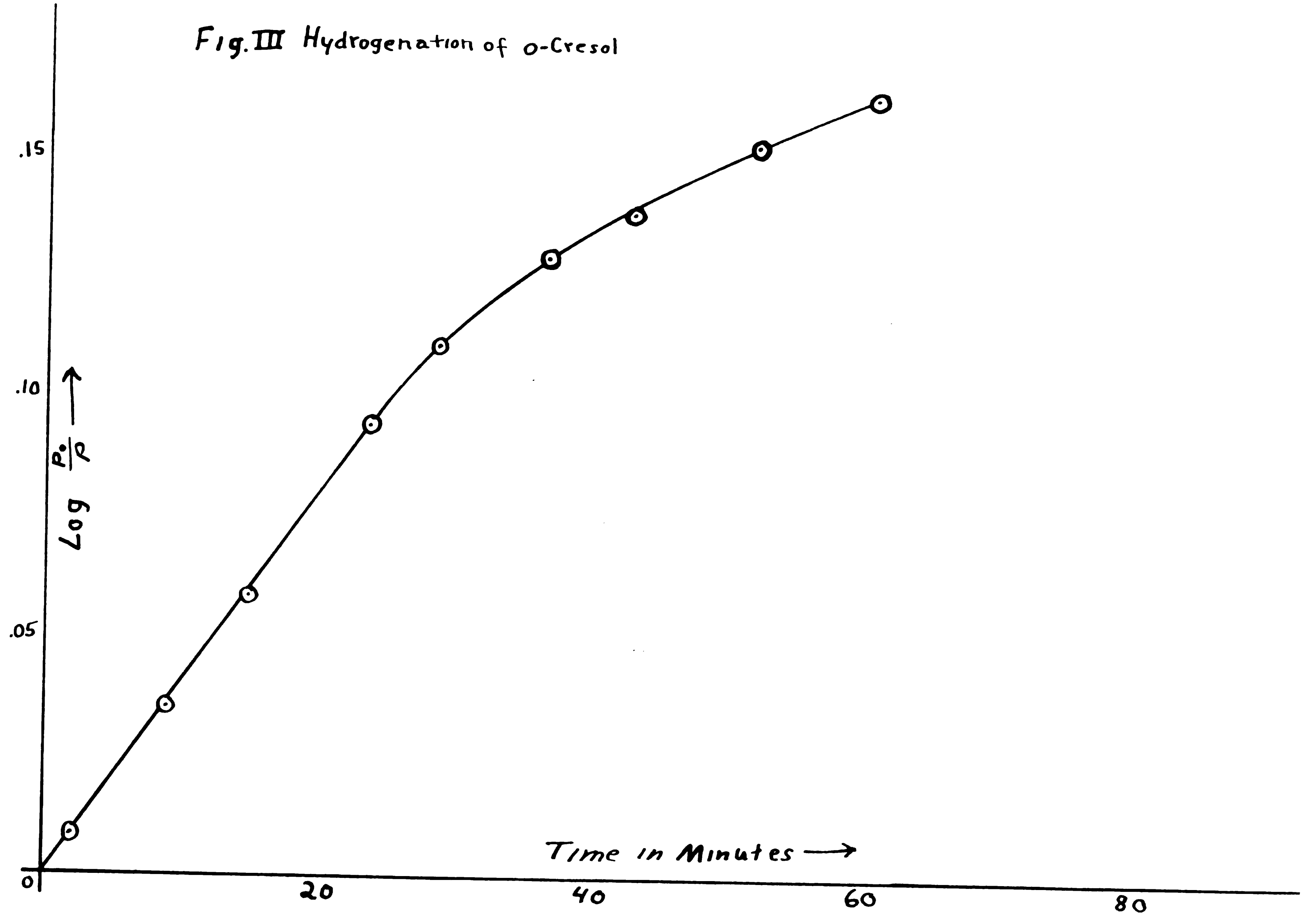


Fig. II Hydrogenation of Cyclohexanone

Fig. III Hydrogenation of o-Cresol



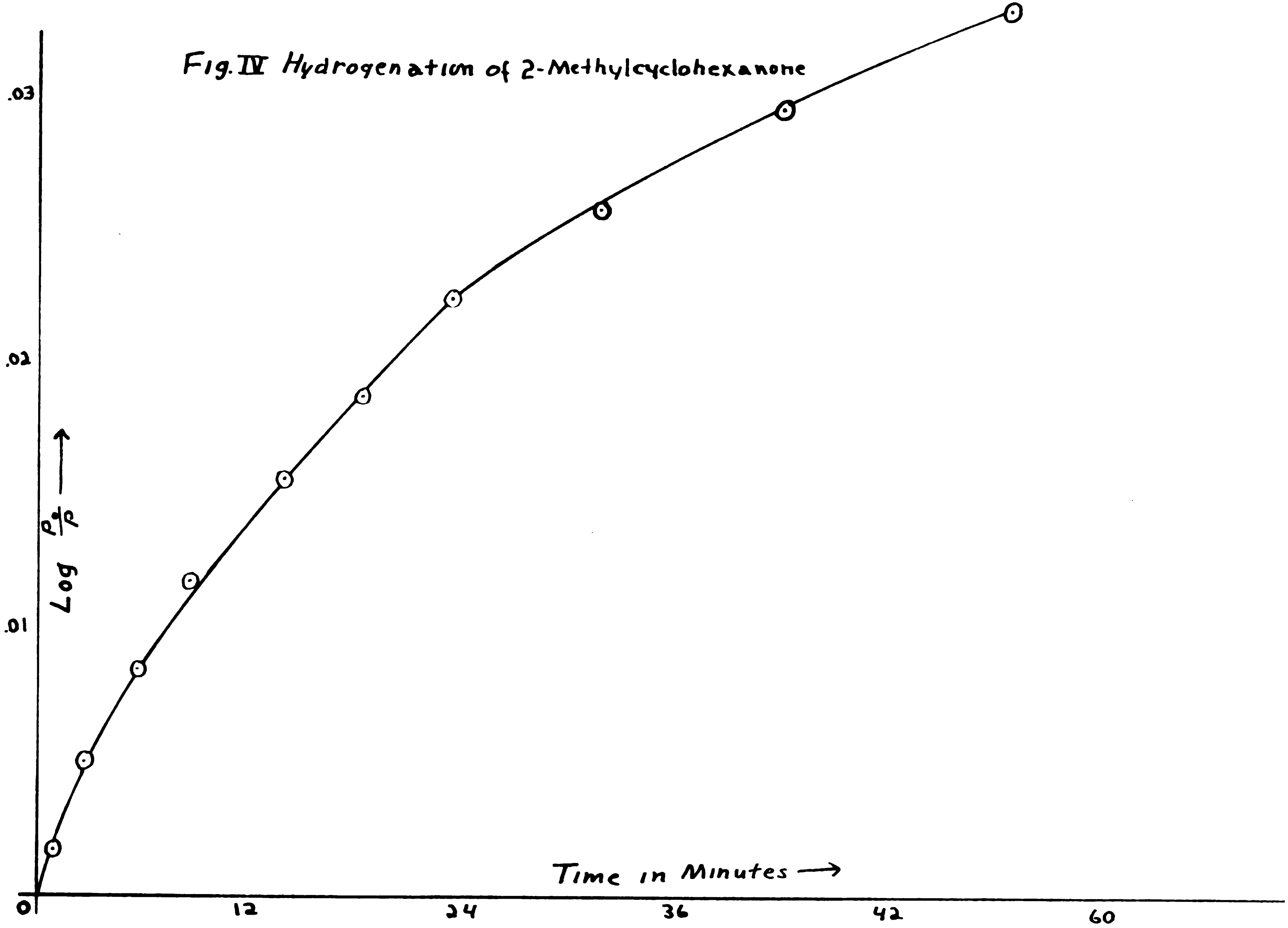


Fig. IV Hydrogenation of 2-Methylcyclohexanone

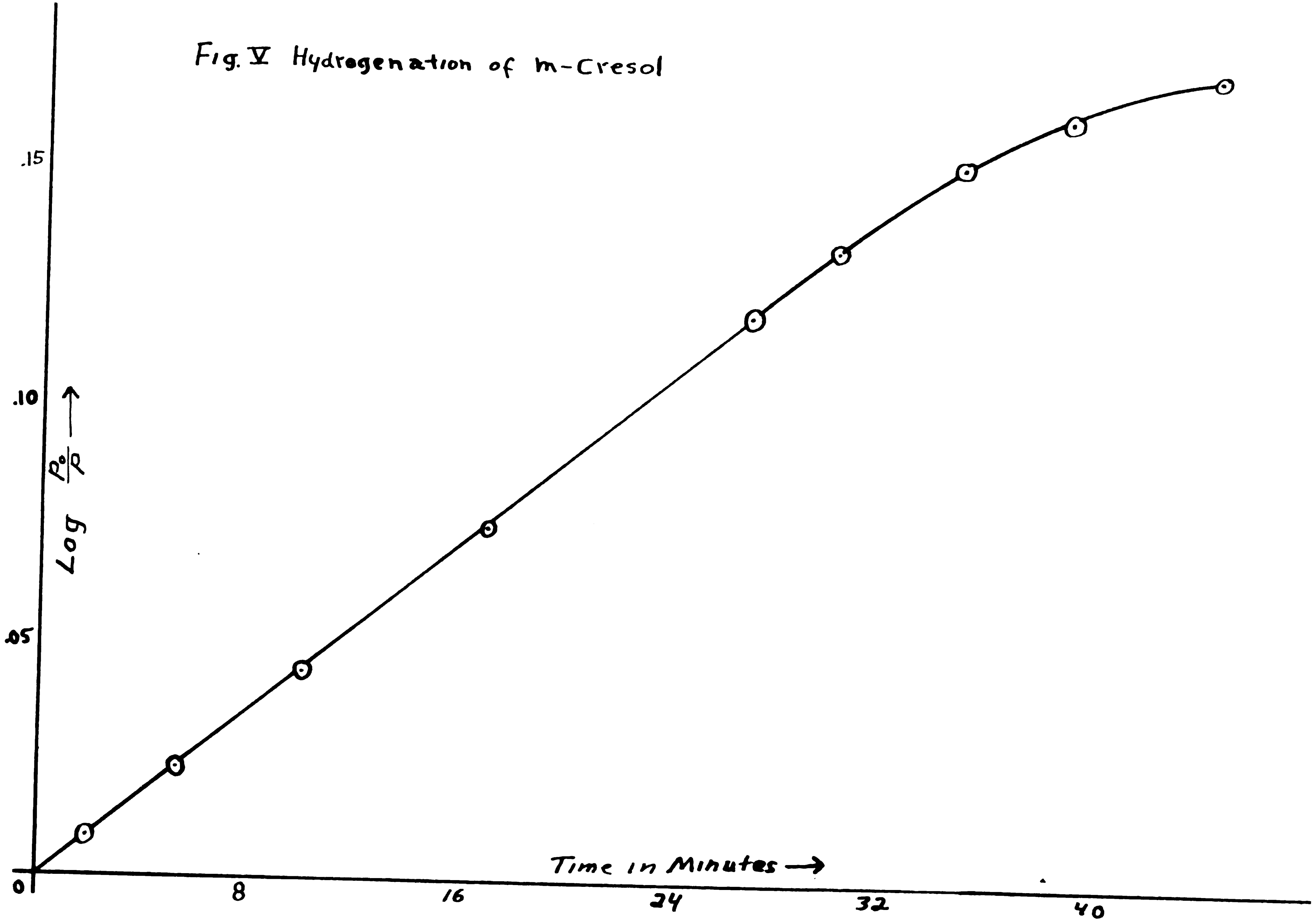


Fig. V Hydrogenation of m-Cresol

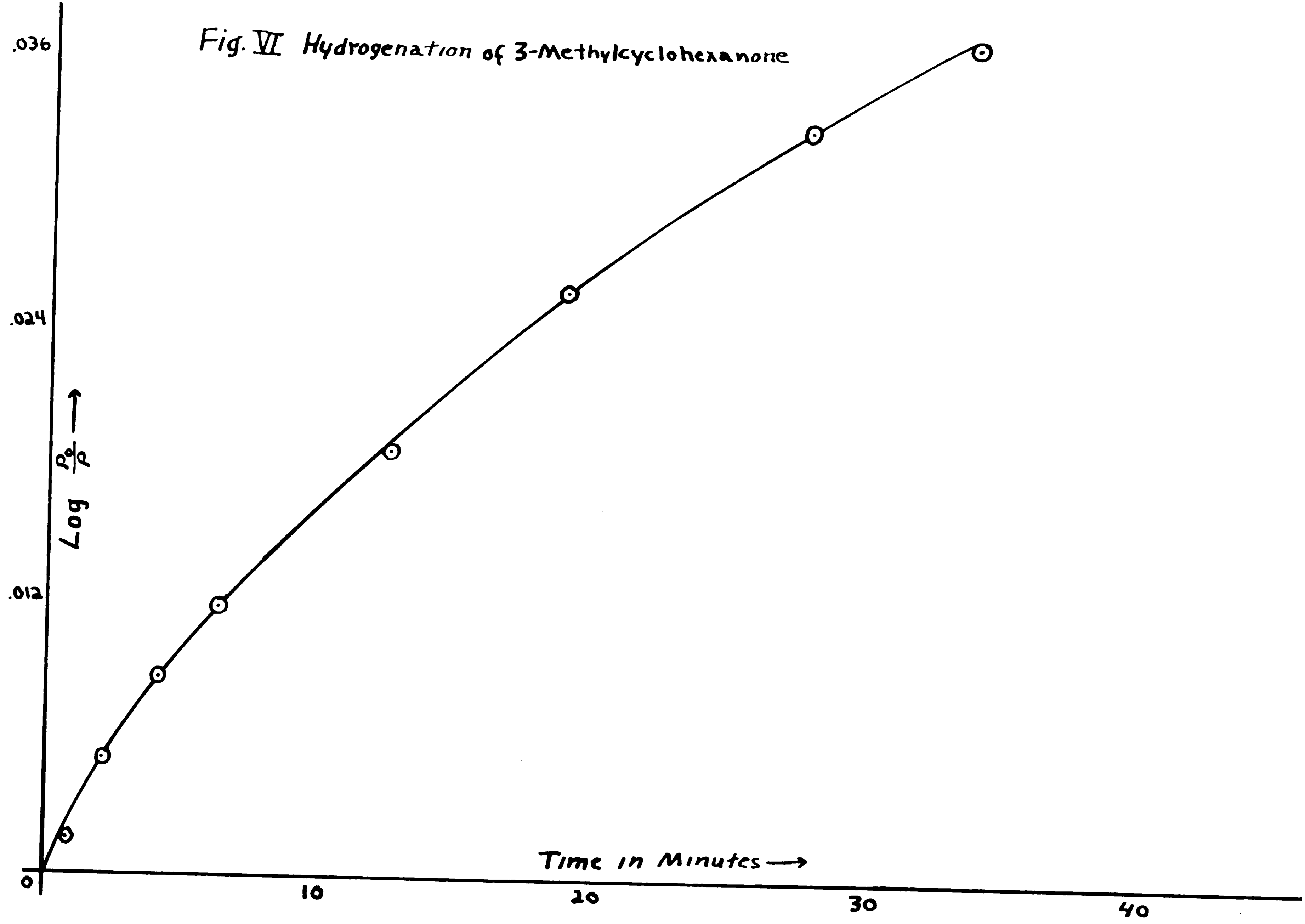


Fig. VI Hydrogenation of 3-Methylcyclohexanone

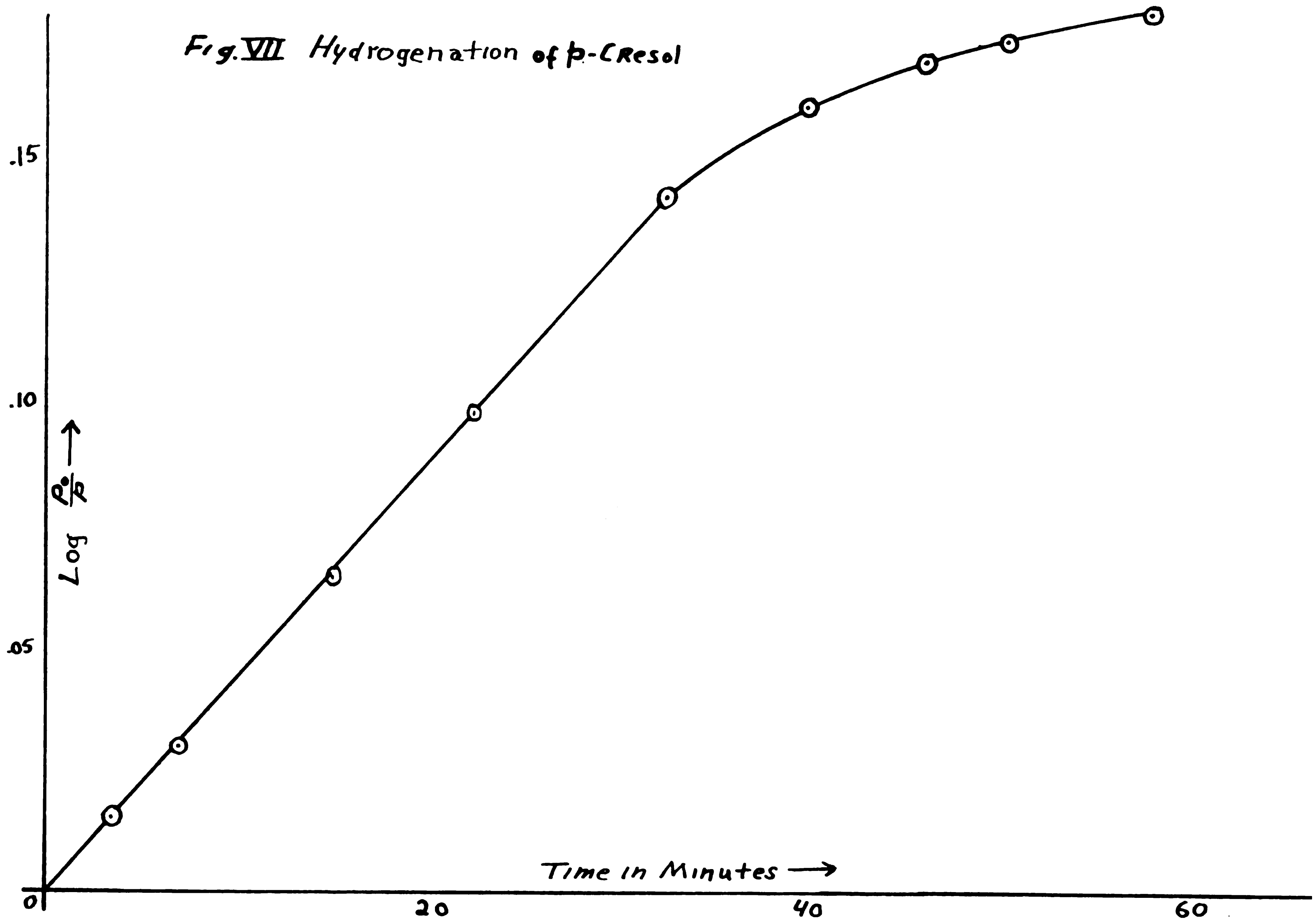


Fig. VII Hydrogenation of p-Cresol

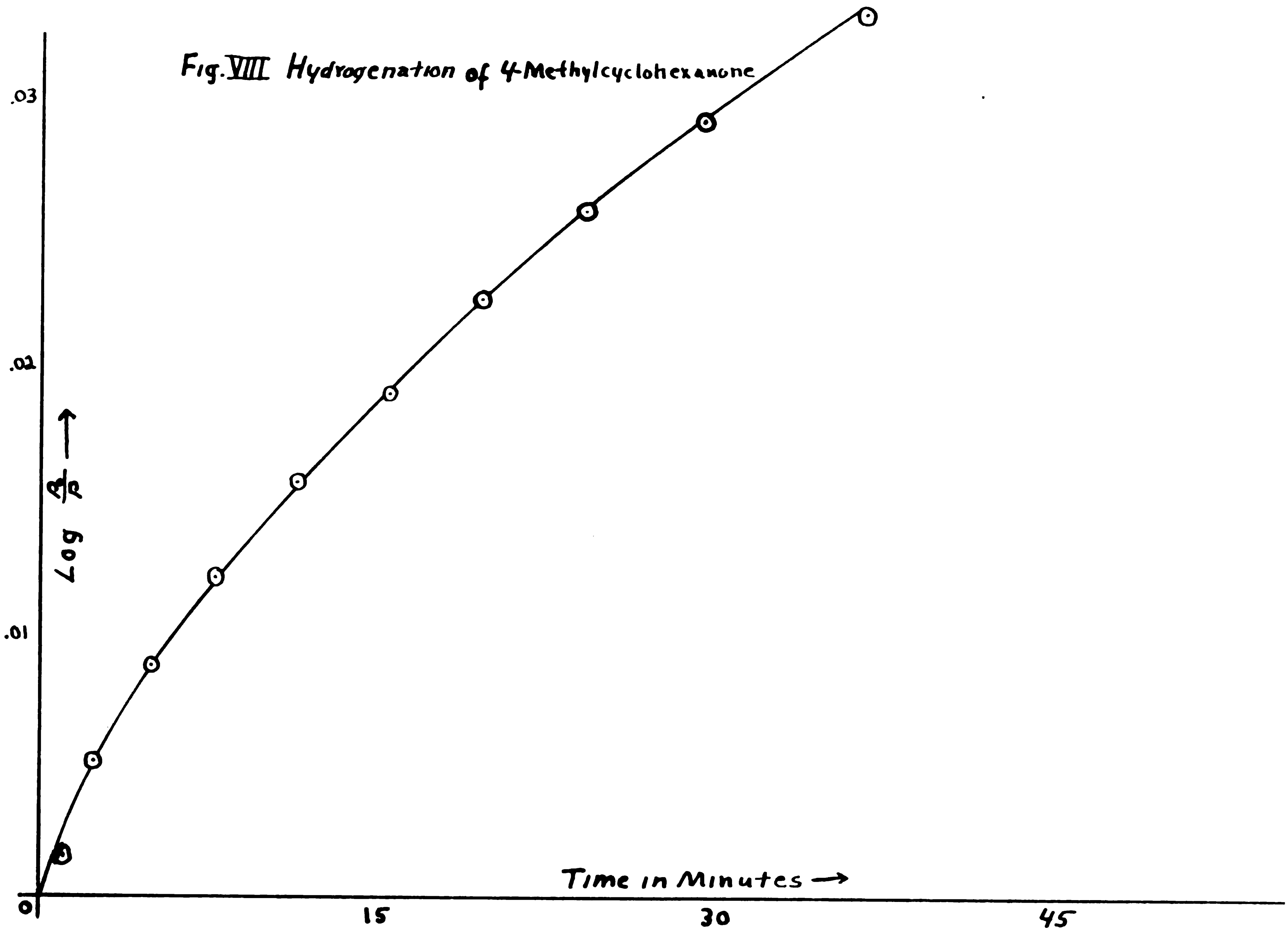


Fig. VIII Hydrogenation of 4-Methylcyclohexanone

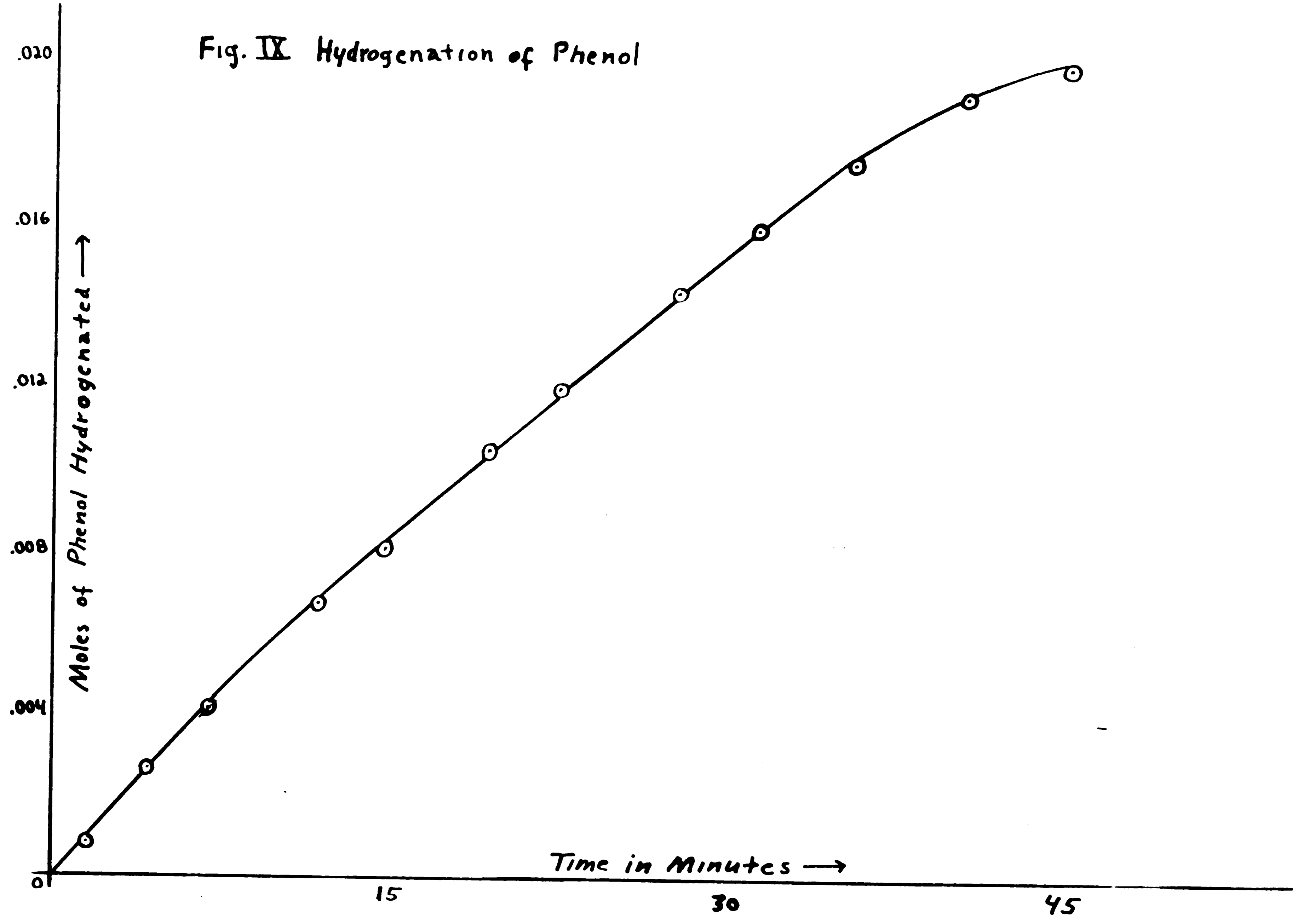


Fig. IX Hydrogenation of Phenol

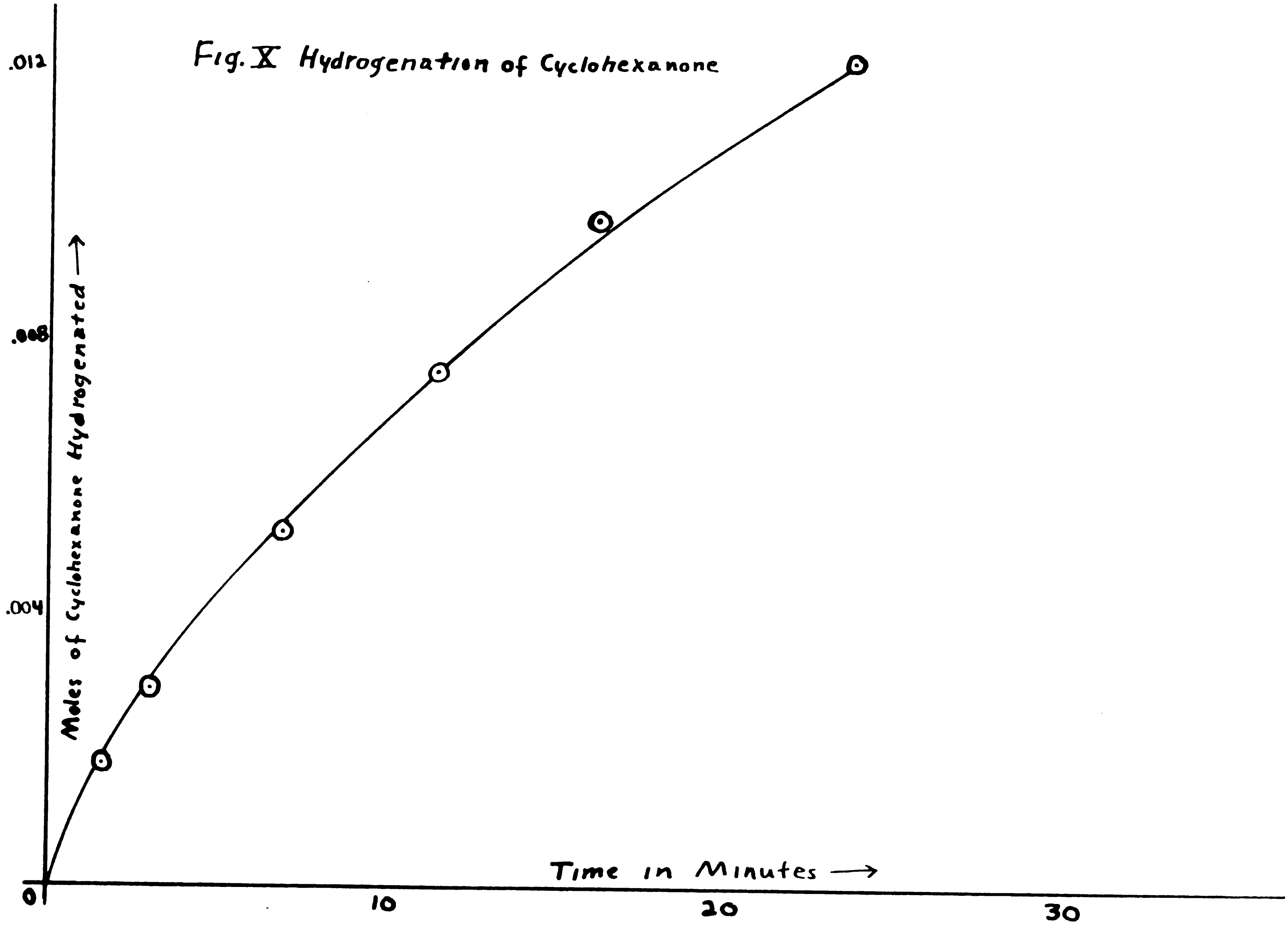


Fig. X Hydrogenation of Cyclohexanone

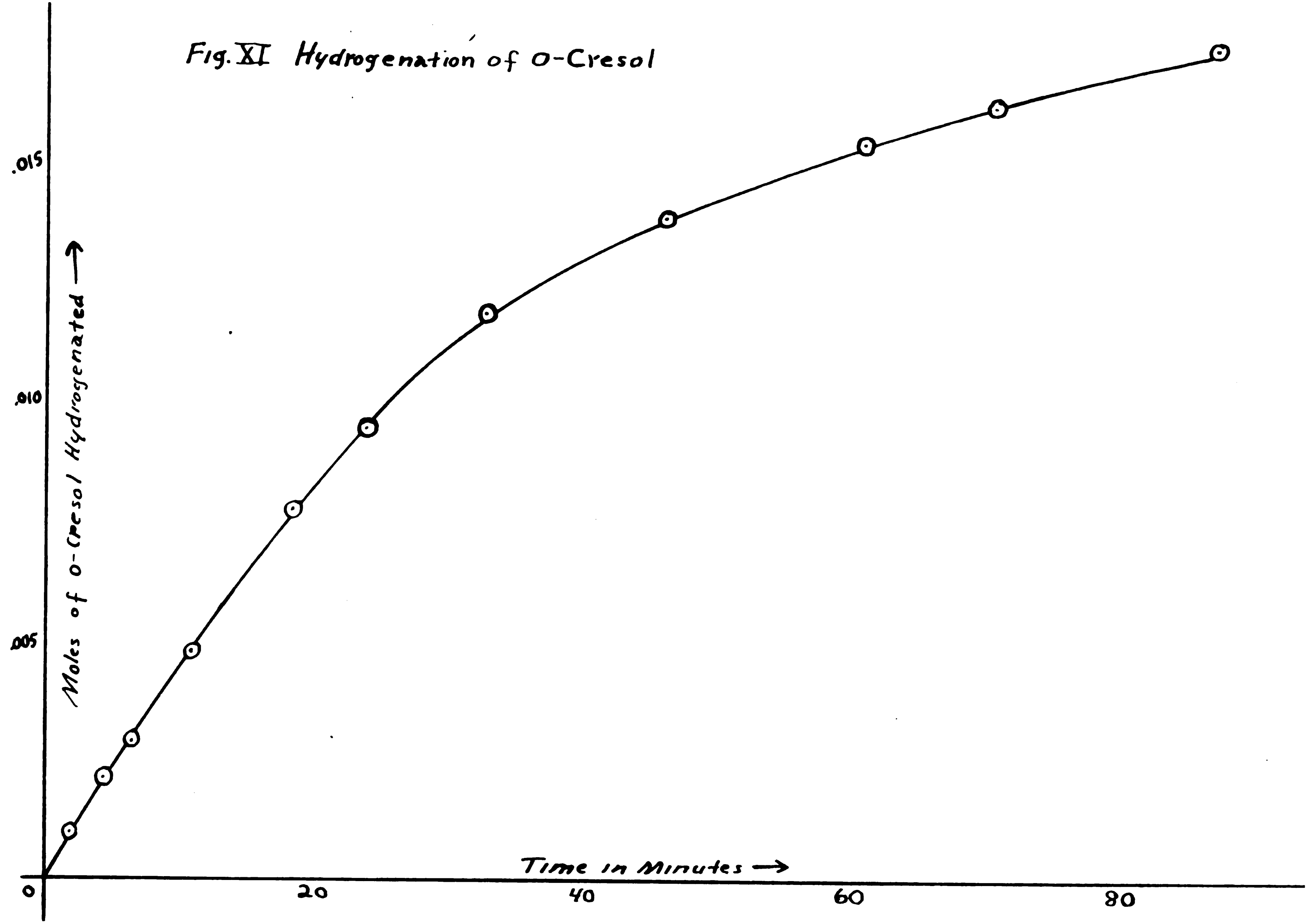


Fig. XI Hydrogenation of O-Cresol

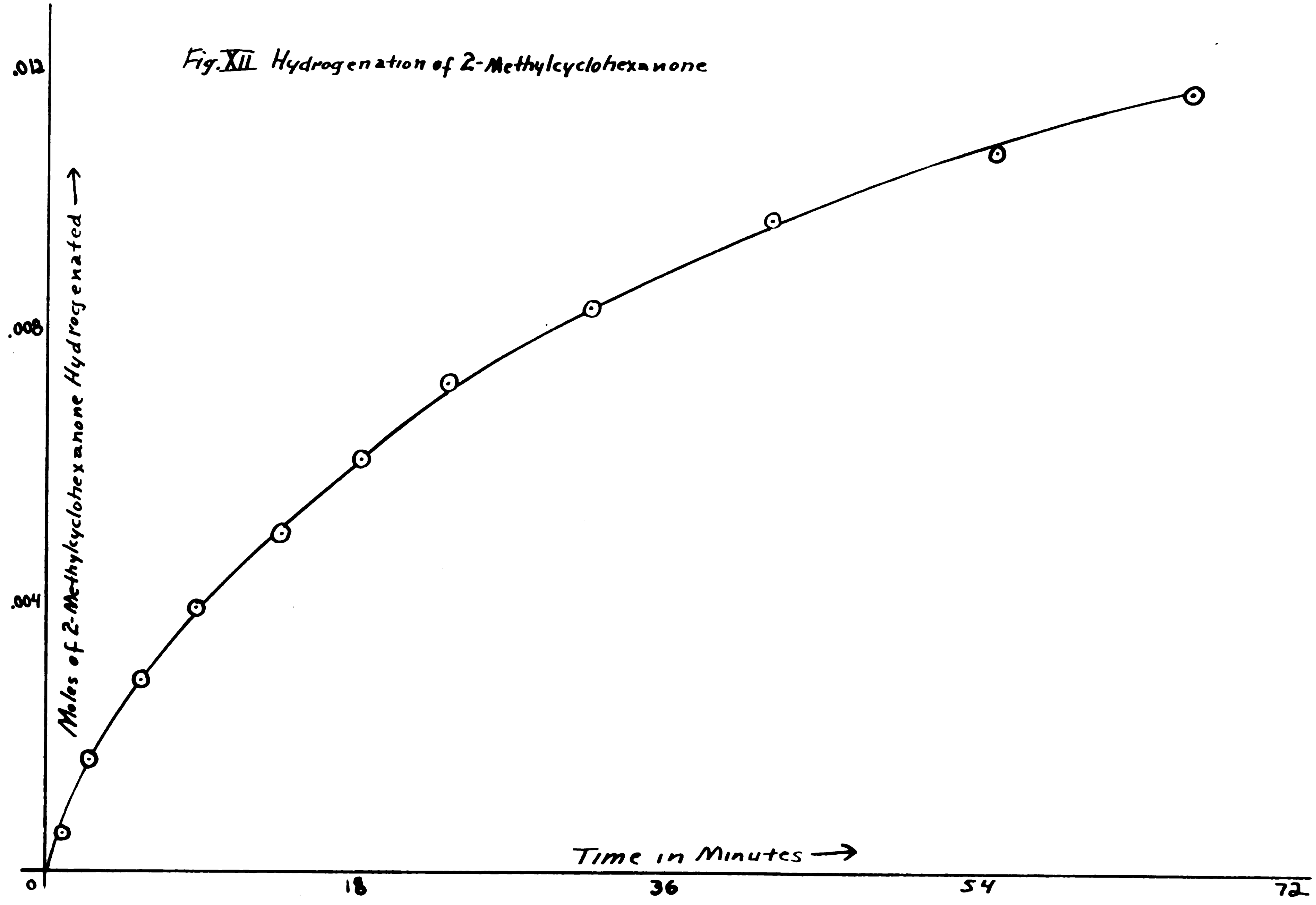


Fig. XII Hydrogenation of 2-Methylcyclohexanone

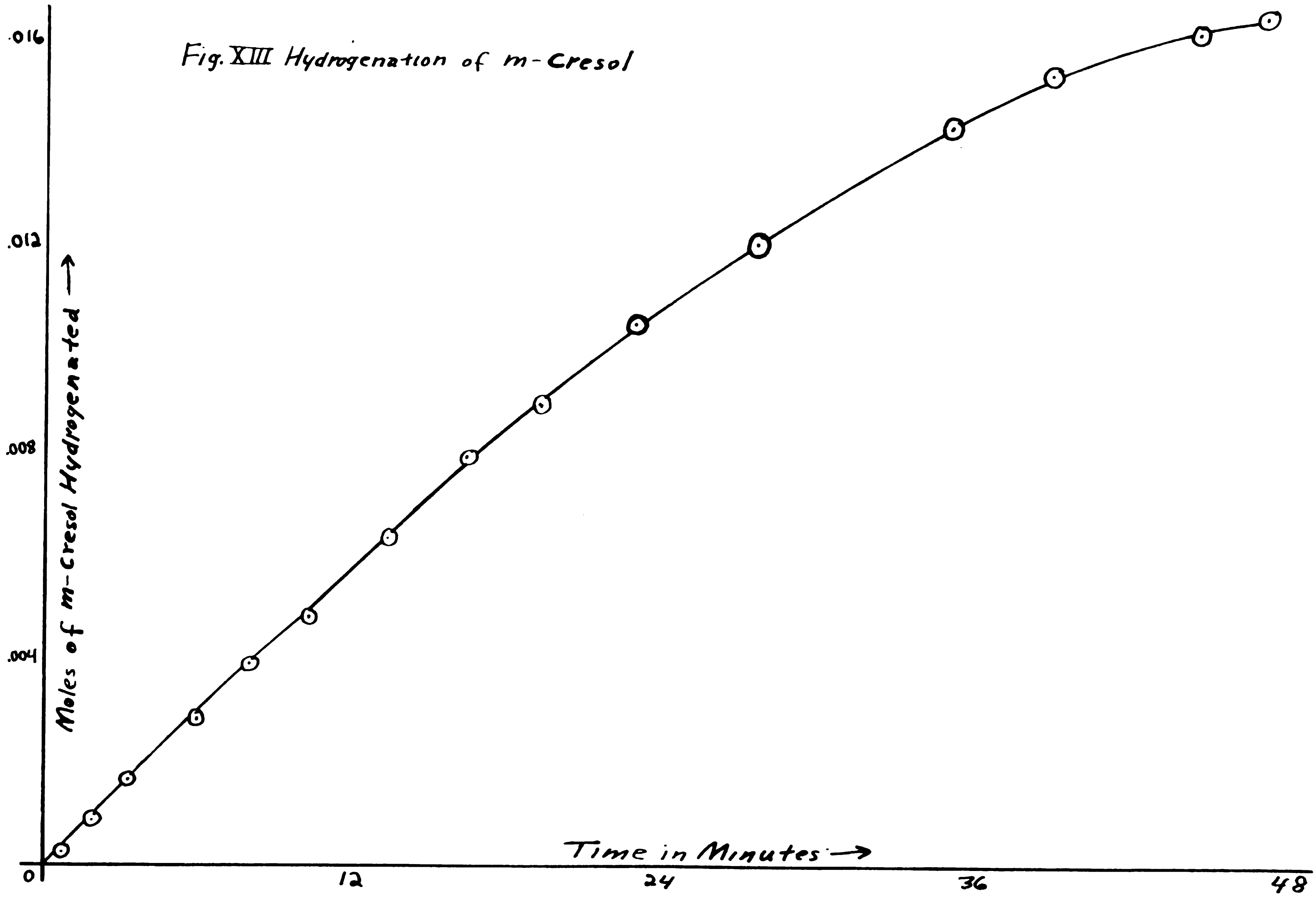


Fig. XIII Hydrogenation of m-Cresol

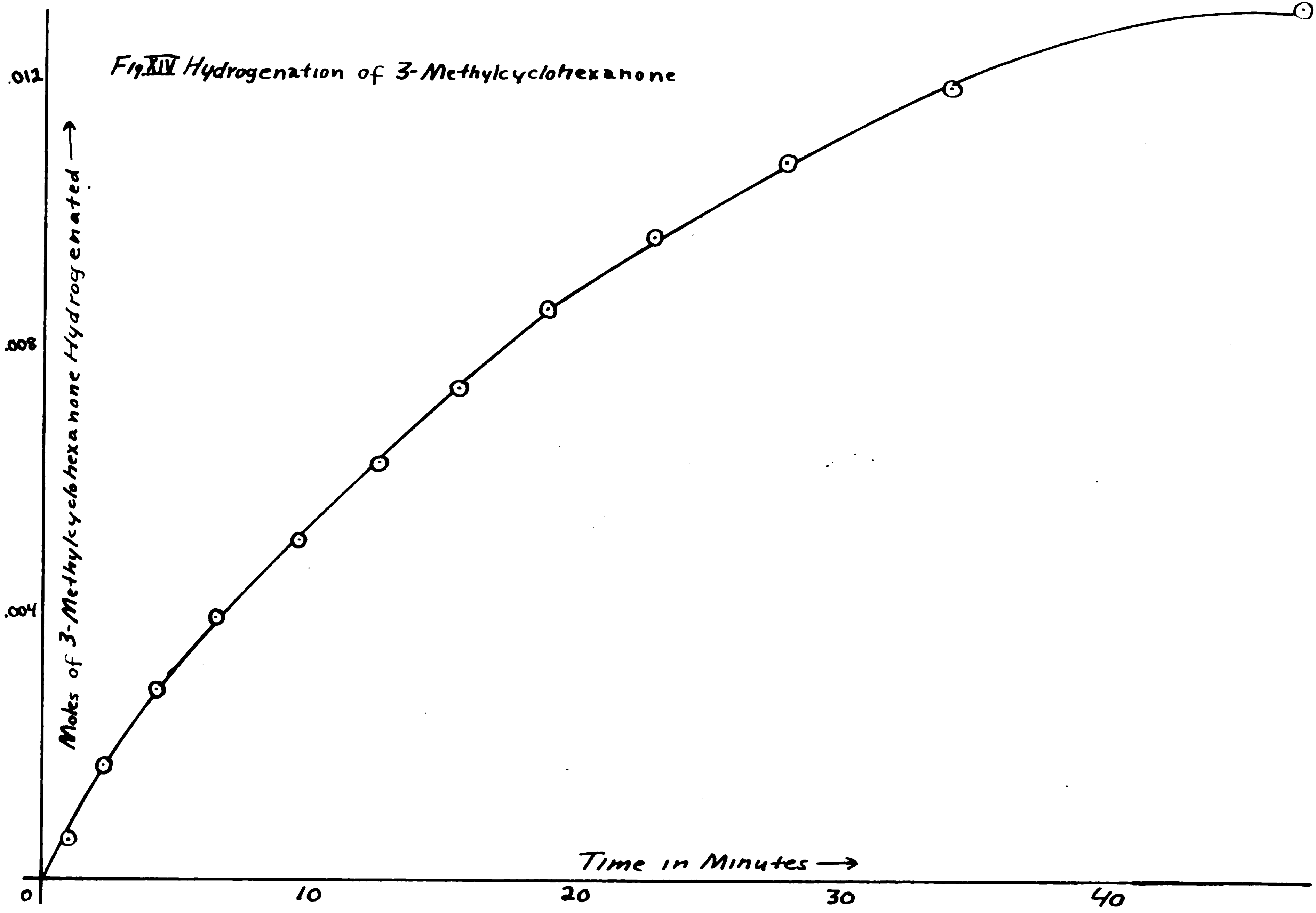


Fig XIV Hydrogenation of 3-Methylcyclohexanone

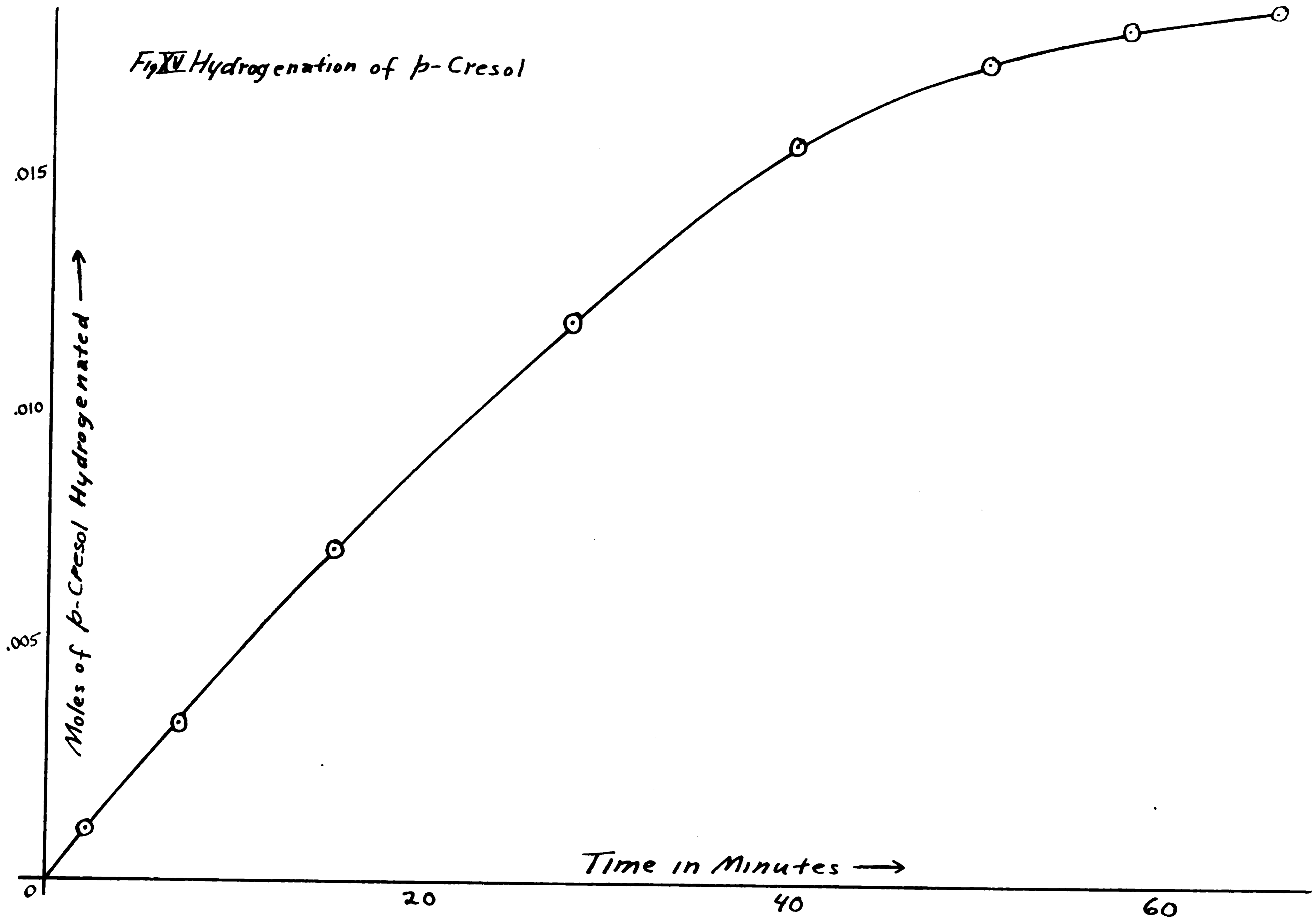


Fig XV Hydrogenation of p-Cresol

Fig. XVI Hydrogenation of 4-Methylcyclohexanone

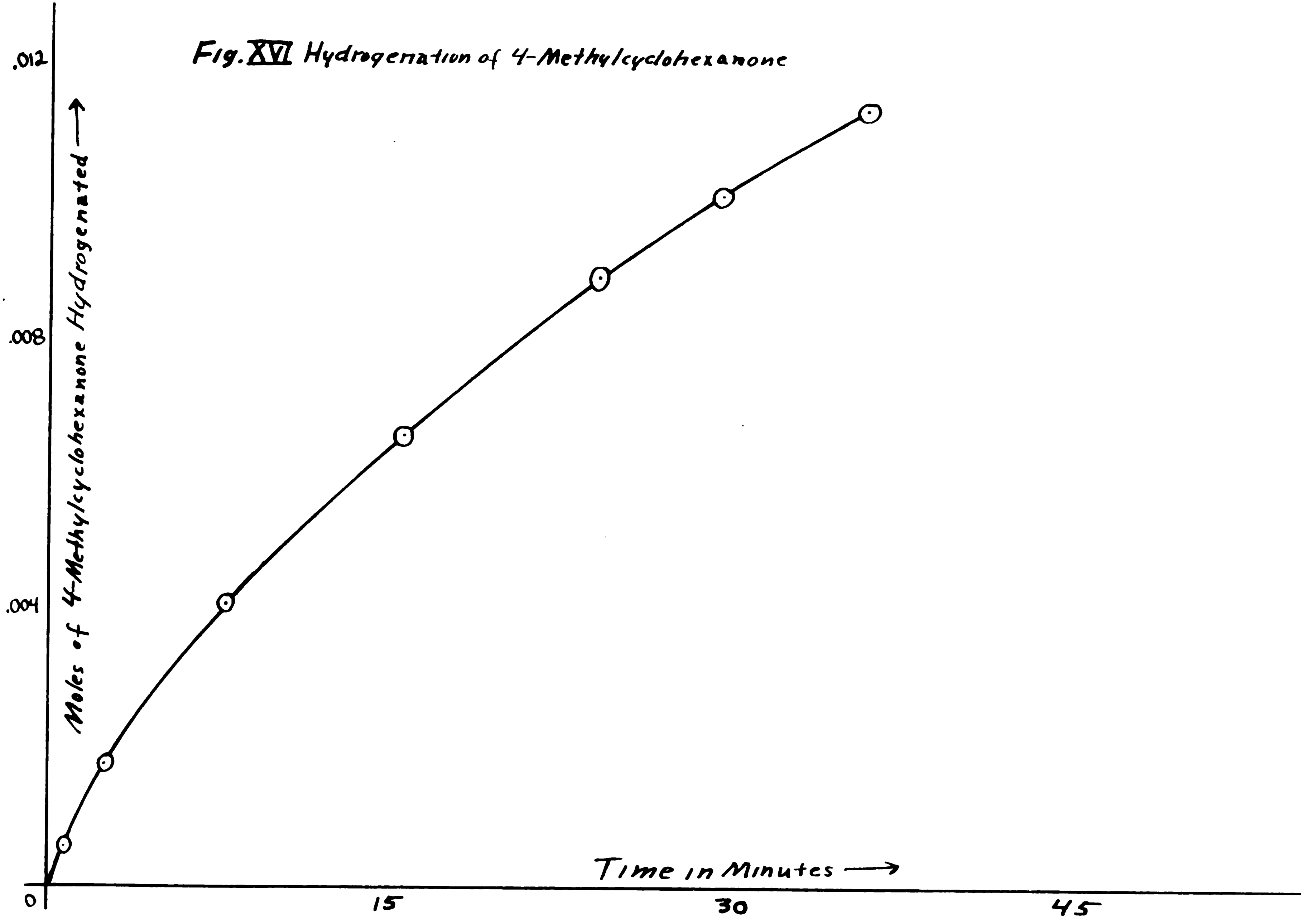
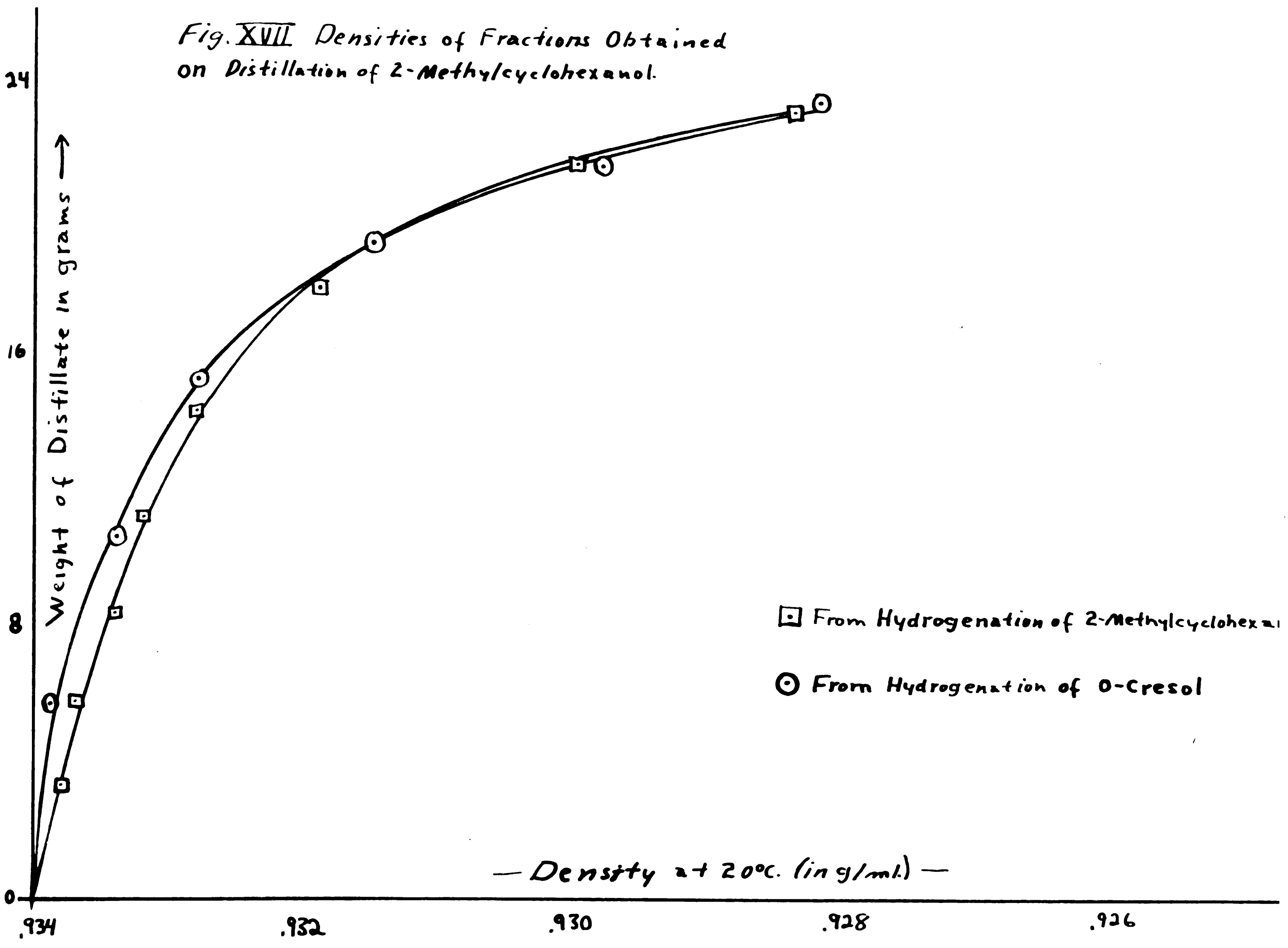


Fig. XVII Densities of Fractions Obtained on Distillation of 2-Methylcyclohexanol.



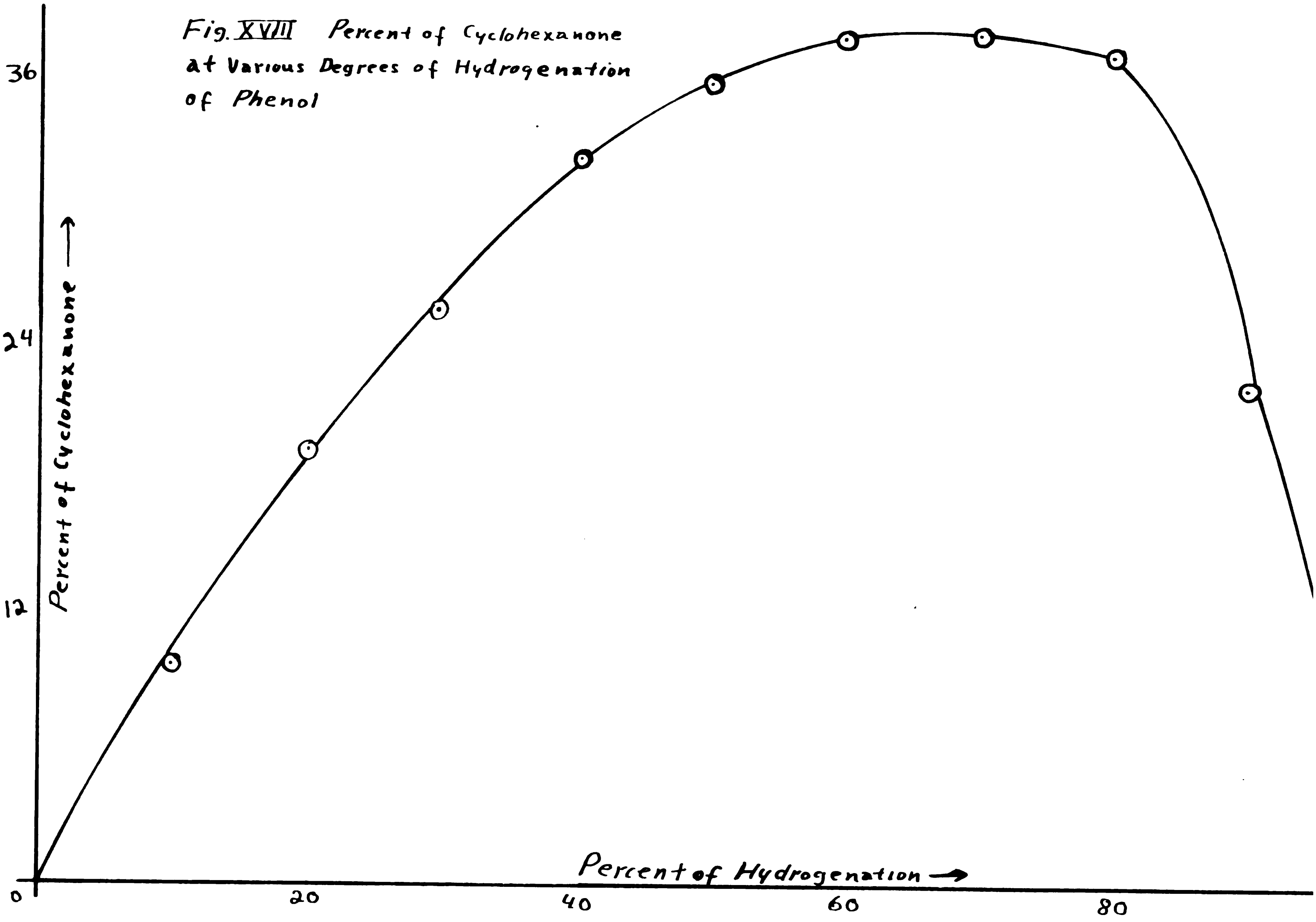


Fig. XVIII Percent of Cyclohexanone at Various Degrees of Hydrogenation of Phenol

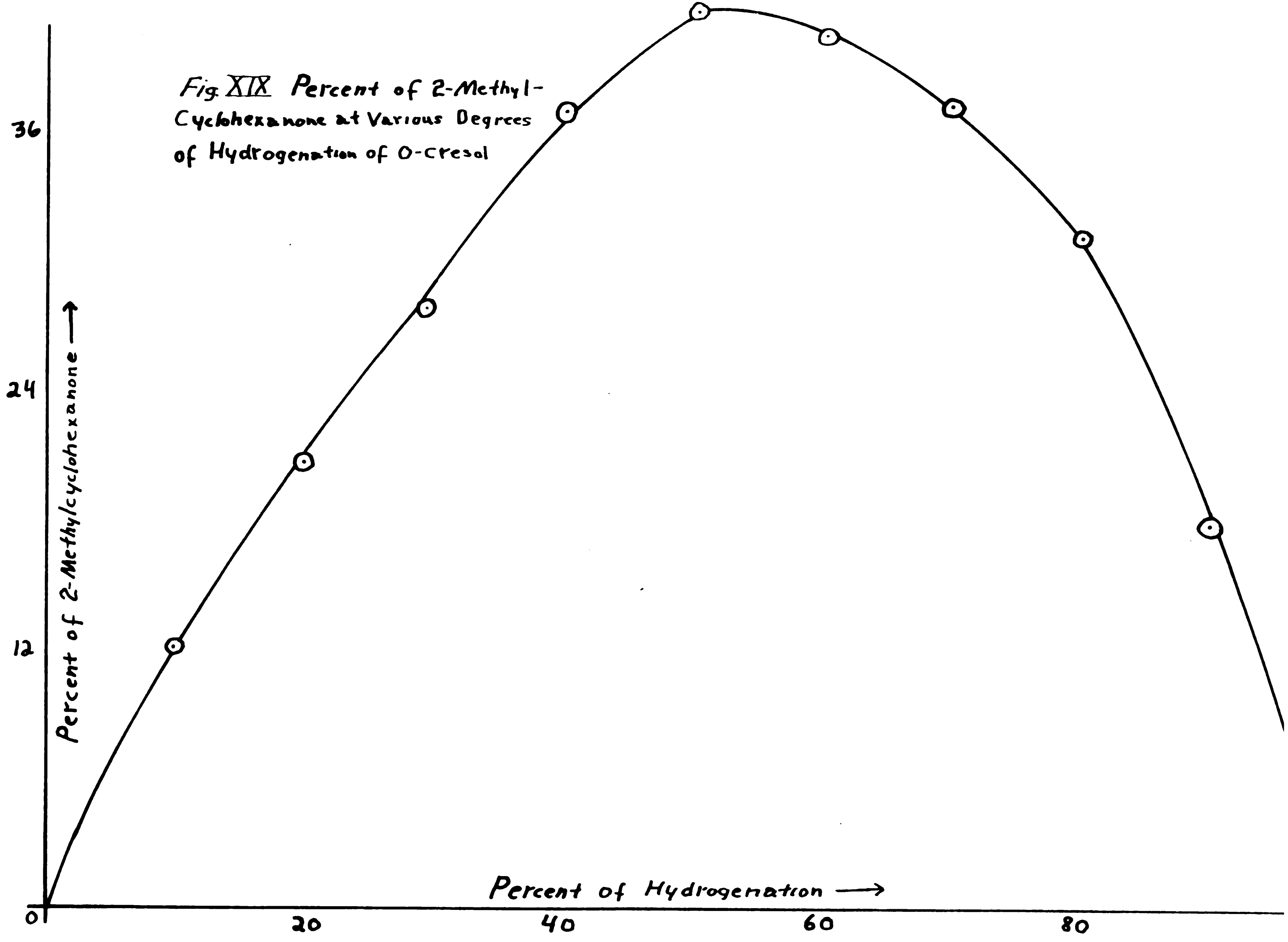


Fig. XIX Percent of 2-Methyl-Cyclohexanone at Various Degrees of Hydrogenation of O-cresol

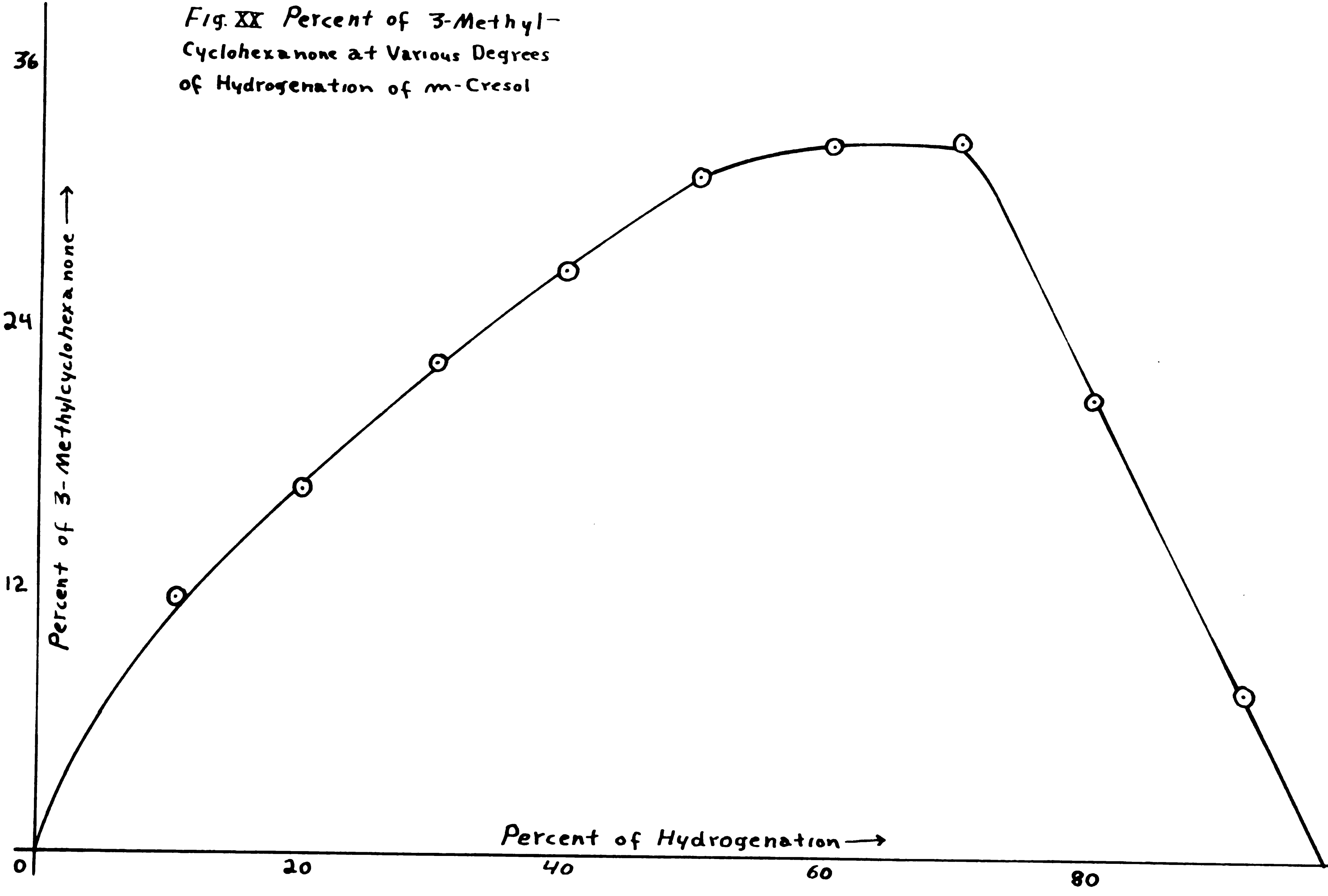


Fig. XX Percent of 3-Methyl-Cyclohexanone at Various Degrees of Hydrogenation of m-Cresol

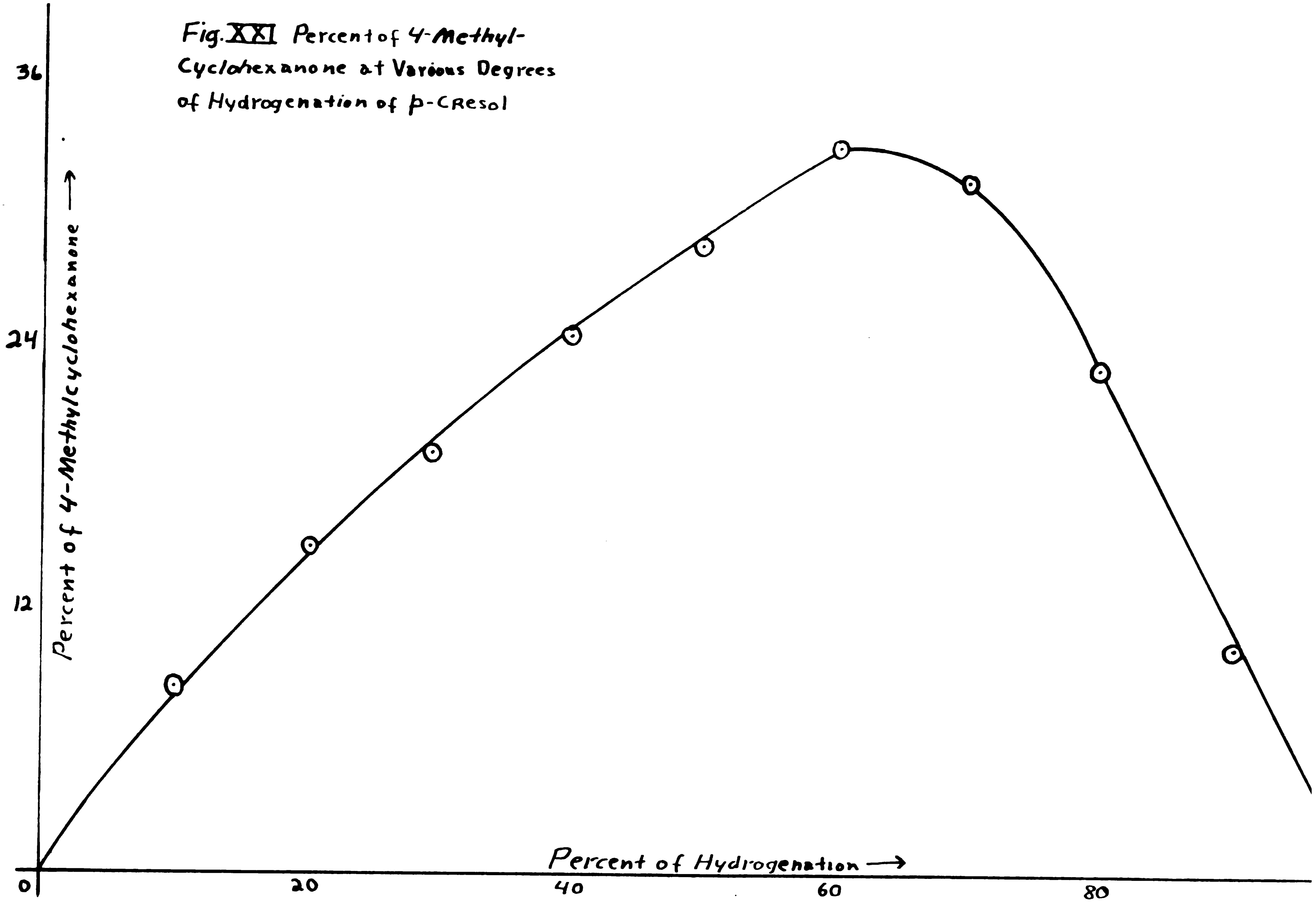


Fig. XXI Percent of 4-Methyl-Cyclohexanone at Various Degrees of Hydrogenation of p-Cresol

Fig. XXII Percent of Components
at Various Degrees of
Hydrogenation of Phenol

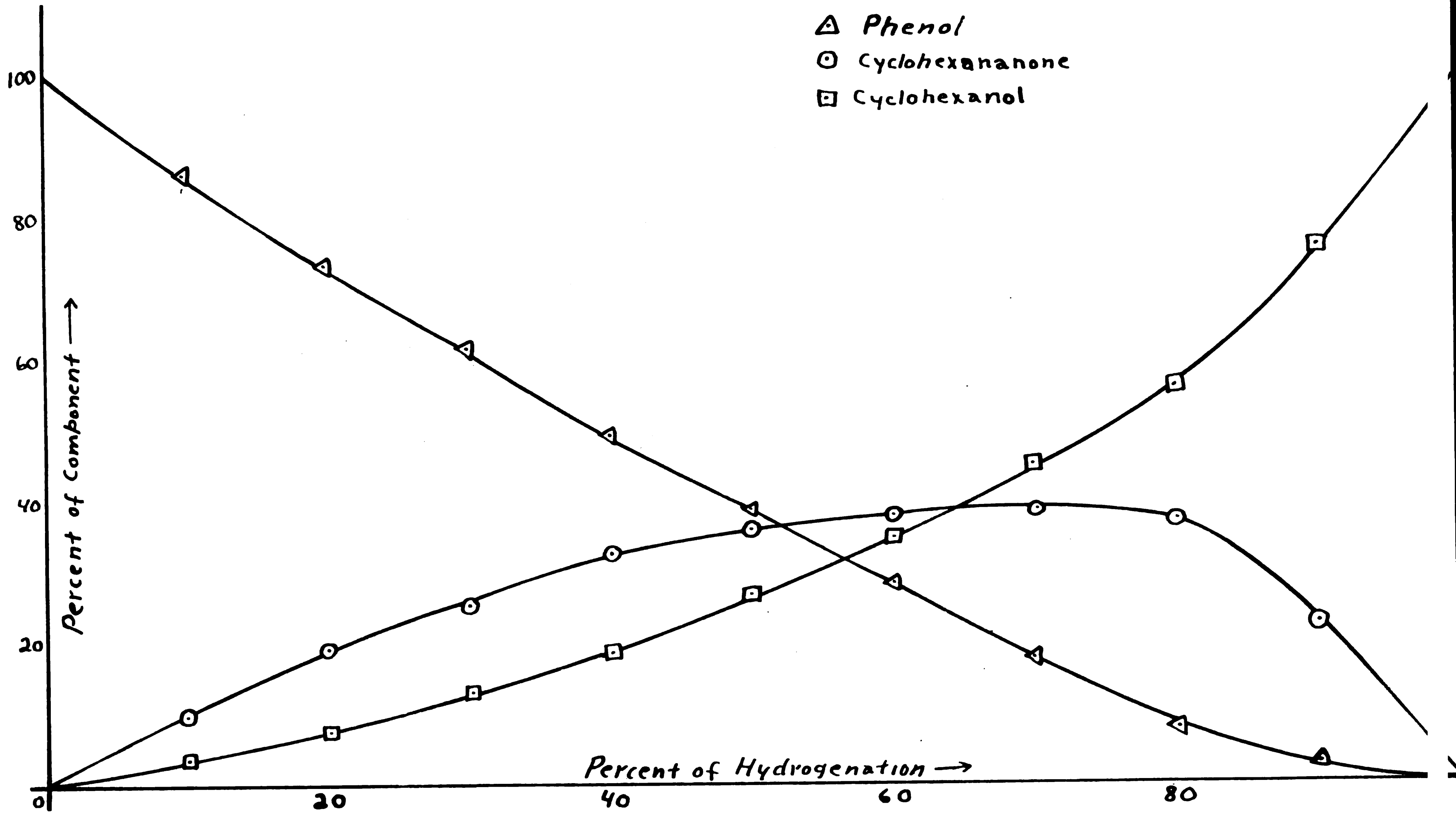


Fig. XXIII Percent of Components at Various Degrees of Hydrogenation of o-Cresol

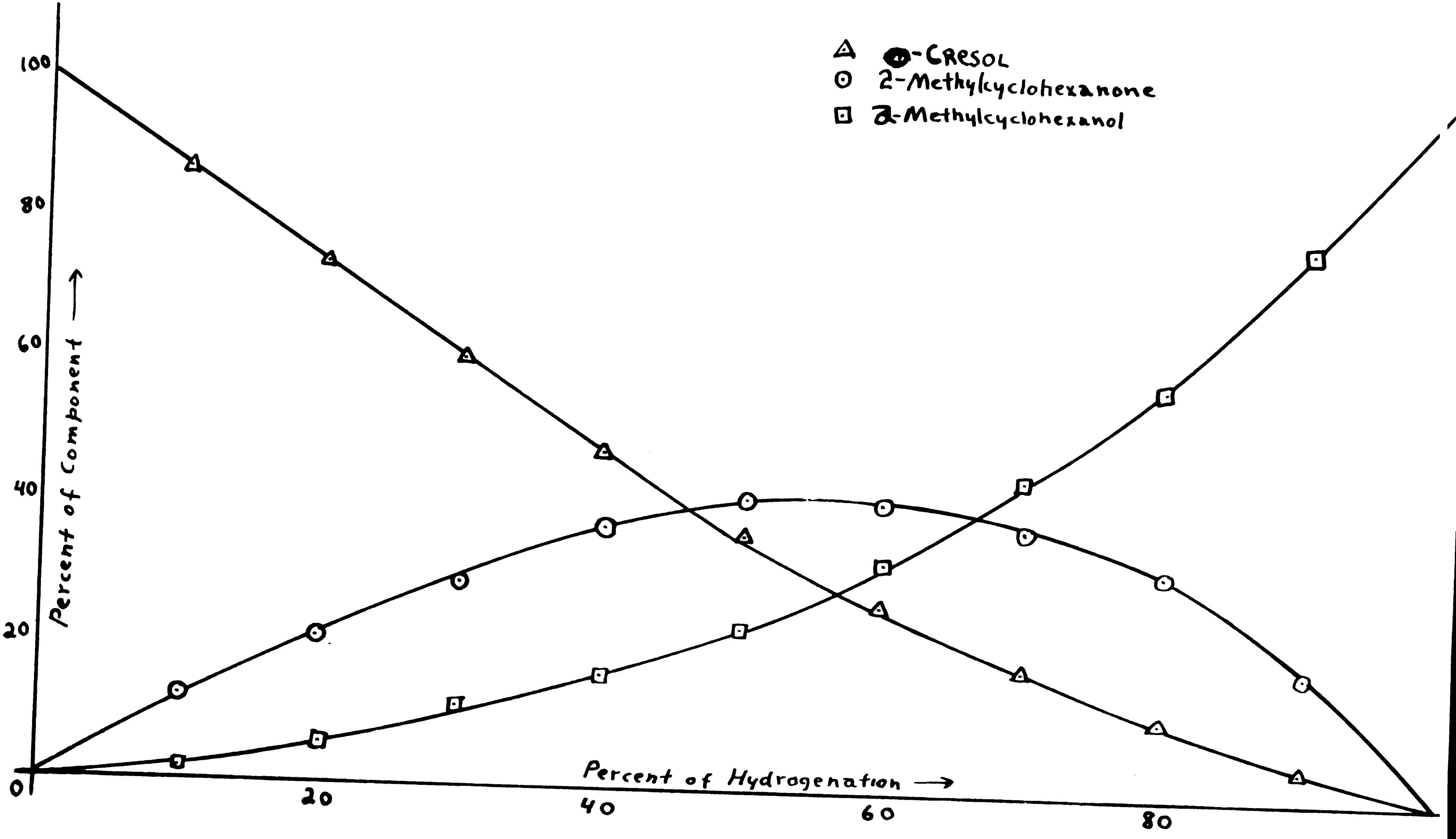


Fig. XXIV Percent of Components
at Various Degrees of
Hydrogenation of m-Cresol

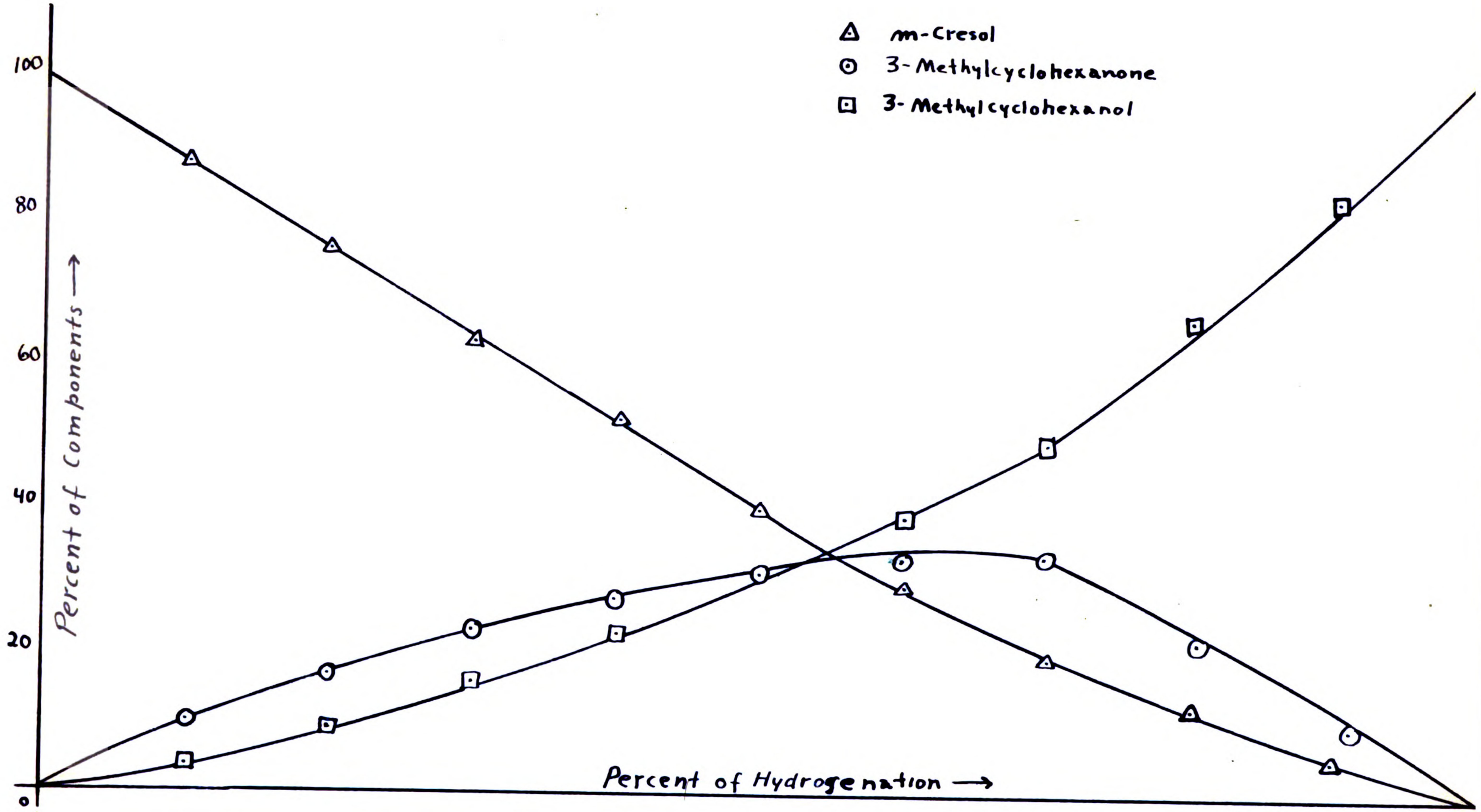
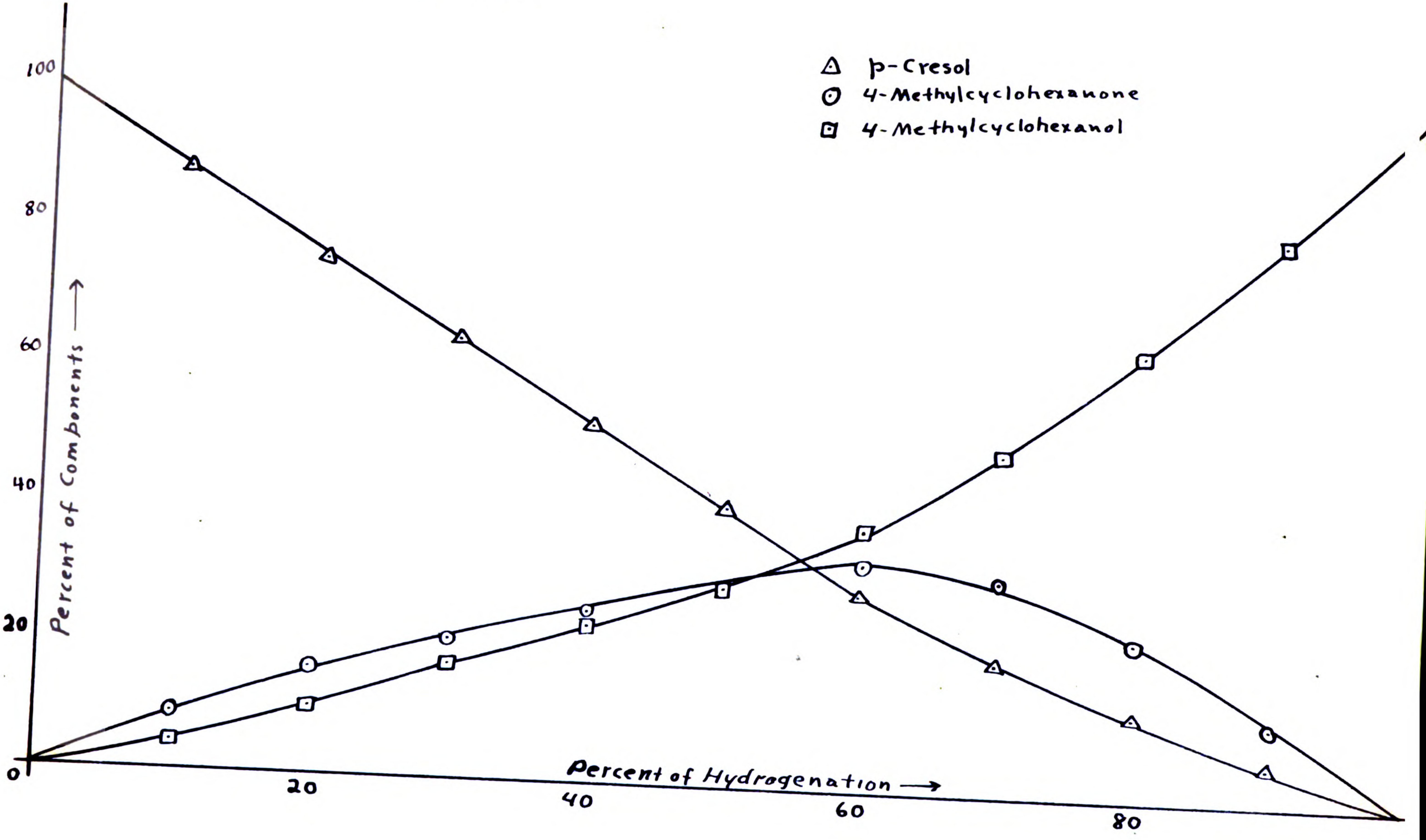


Fig. XXV Percent of Components at Various Degrees of Hydrogenation of p-Cresol



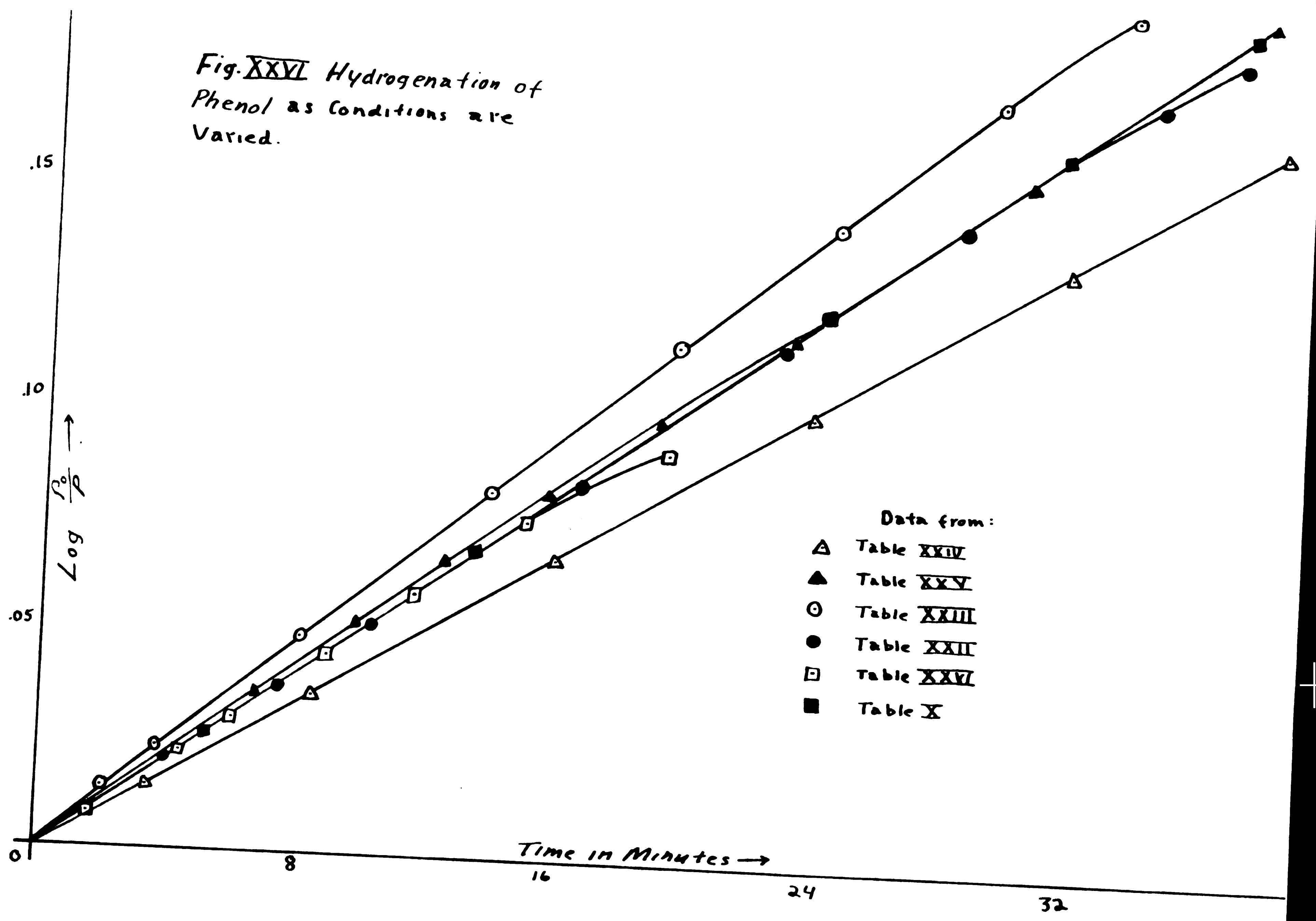


Fig. XXVI Hydrogenation of Phenol as Conditions are Varied.

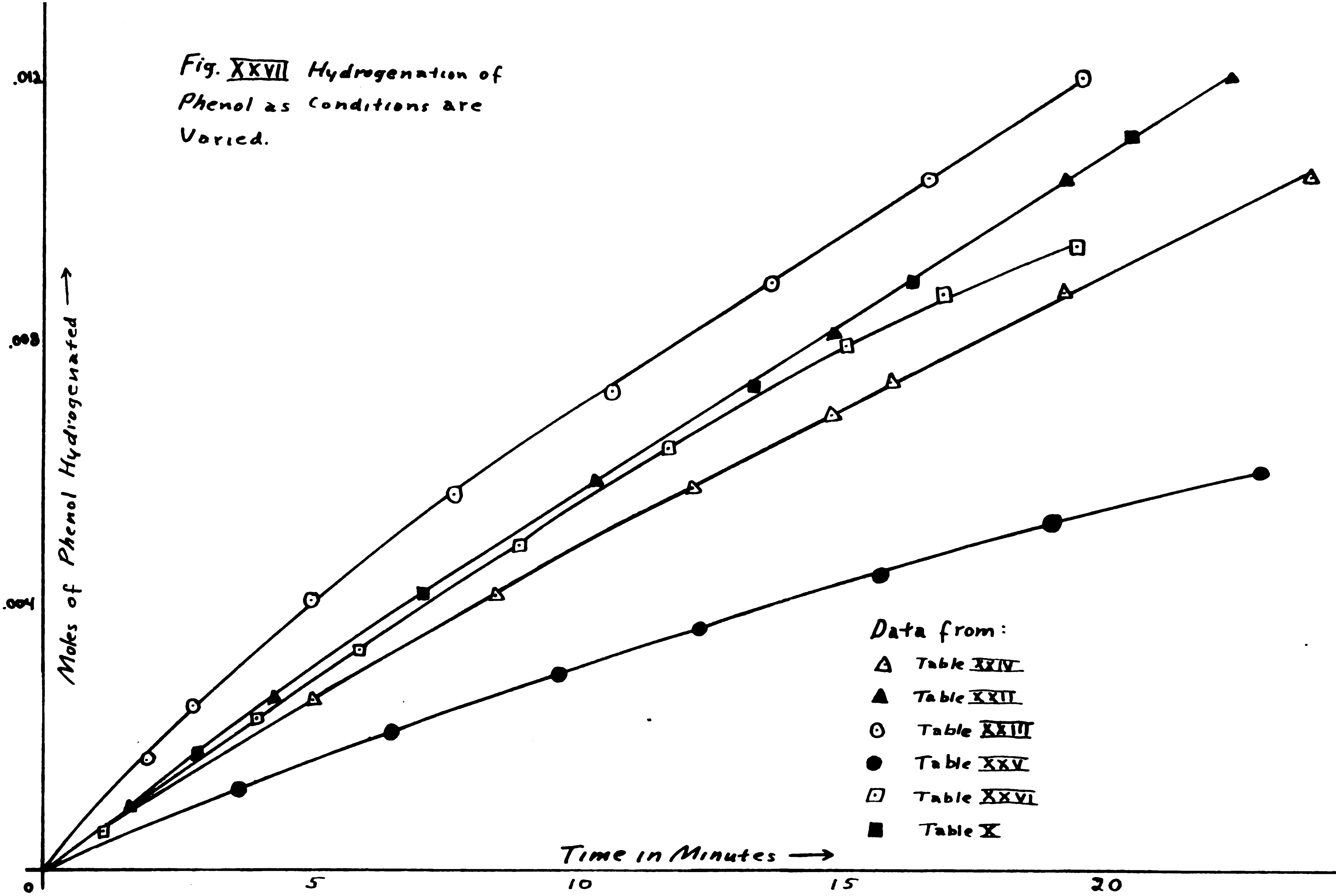


Fig. XXVII Hydrogenation of Phenol as Conditions are Varied.

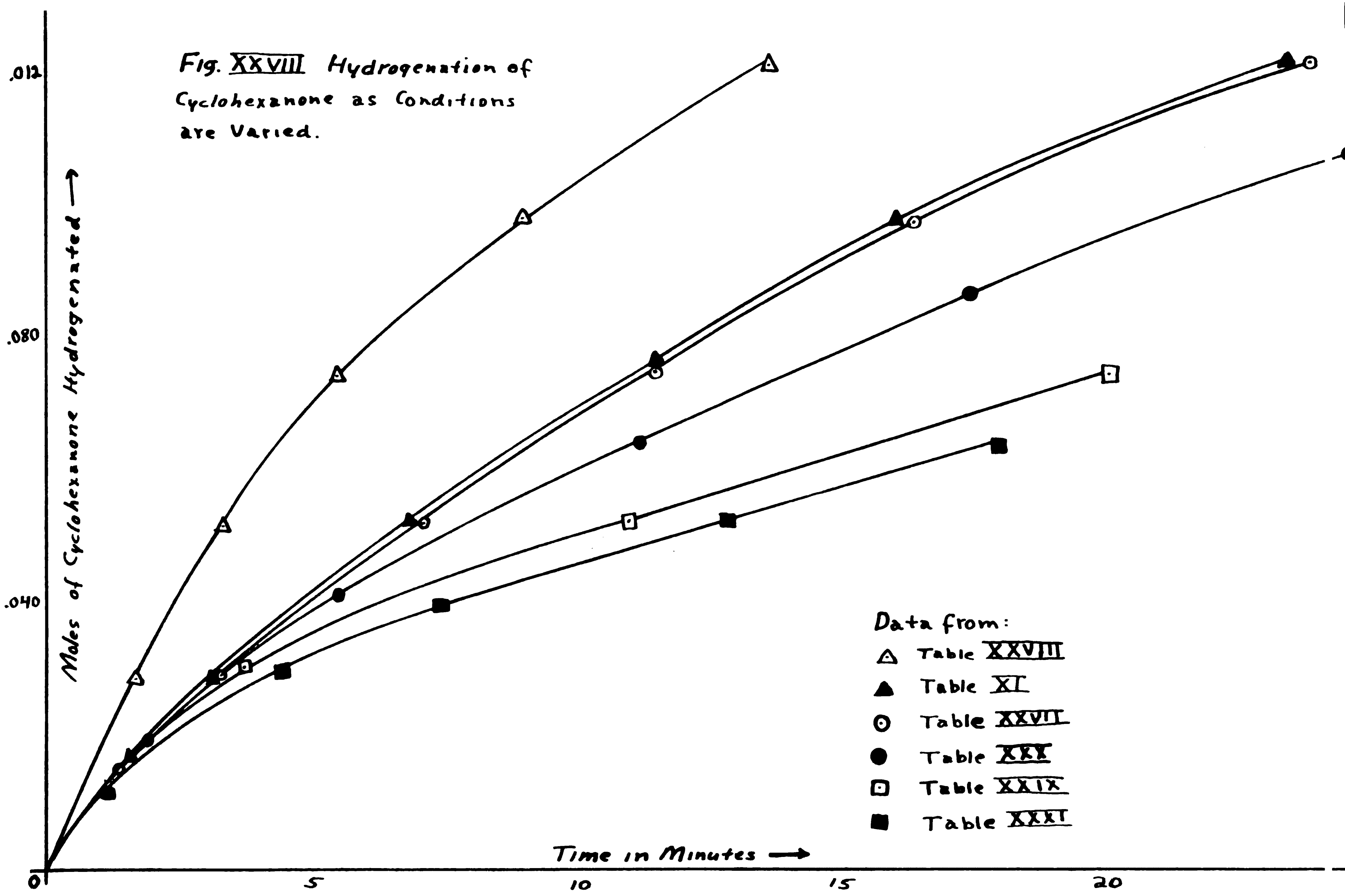


Fig. XXVIII Hydrogenation of Cyclohexanone as Conditions are Varied.

VITA

Name: Arthur F. Miller

Born: November 15, 1925 in Ashtabula, Ohio

Academic Career:
Ashtabula High School, Ashtabula, Ohio, 1940-1943
Bowling Green State University, Bowling Green, Ohio, 1946-1950
Michigan State College, East Lansing, Michigan, 1950-1953

Degrees Held: B. S. Bowling Green State University, 1950